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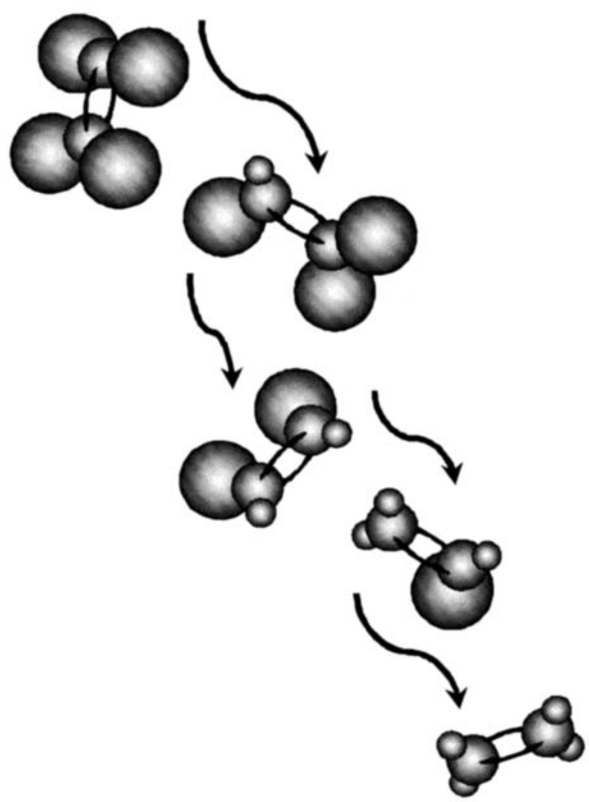
FINAL REPORT

SERDP/ESTCP Expert Panel Workshop on Research and Development Needs for Cleanup of Chlorinated Solvent Sites



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14. ABSTRACT
The Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) are designed to develop and transition innovative research and technology to help the Department of Defense (DoD) perform its mission. These programs together conducted an expert panel workshop on August 6-7, 2001 to evaluate the needs for research and development in the general area of chlorinated solvent site cleanup. This area is a major focus for both programs, and this workshop was held to help establish the funding priorities for the coming years.

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Mention of any trade names in this report does not imply endorsement. The cover page illustration is taken from *Engineered Approaches to In Situ Bioremediation of Chlorinated Solvents: Fundamentals and Field Applications* (EPA 542-R-00-008, July 2000).

List of Attachments

1 Introduction

The Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) are designed to develop and transition innovative research and technology to help the Department of Defense (DoD) perform its mission. These programs together conducted an expert panel workshop on August 6-7, 2001 to evaluate the needs for research and development in the general area of chlorinated solvent site cleanup. This area is a major focus for both programs, and this workshop was held to help establish the funding priorities for the coming years.

Environmental cleanup is one of the major thrust areas in the SERDP/ESTCP programs (the others are pollution prevention, compliance, conservation, and unexploded ordnance). Although DoD facilities have numerous types of contaminants, chlorinated solvents are by far the most prevalent, particularly trichloroethylene (TCE) and perchloroethylene (PCE), but related compounds such as trichloroethane (TCA), vinyl chloride (VC), dichloroethenes (DCE), and carbon tetrachloride (CT) also represent significant concerns. These chlorinated aliphatic hydrocarbons (CAHs) also remain among the most difficult to remediate, despite several years of research and development.

This workshop was intended to develop a strategic plan to guide research and technology development in the next 5-10 years. The overall objective was to provide guidance on how these programs can best invest their limited research, development, and demonstration funds to improve DoD's ability to effectively address its CAH- contaminated sites. The workshop participants were asked to identify the major basic and applied research, development, and demonstration needs, the specific technical issues that must be addressed to meet regulatory and other stakeholder concerns, and the major gaps in our scientific understanding of CAH contamination and cleanup. Further, the participants were asked to prioritize these research and development needs and identify those areas with the greatest promise to help DoD accomplish its goals.

2 Process

The workshop was held in Chantilly, VA and spanned two full days. Prior to the meeting an agenda was prepared, and the participants were identified (Attachment A). The participants included leaders in the general topic area, and individuals were selected to represent various key disciplines. Participants were also selected to represent leaders in both science and technology, to ensure that both more basic and more applied perspectives were included.

A white paper was prepared and distributed to the participants before the workshop (Attachment B). This white paper was intended to frame the key questions that the workshop needed to address, to establish common terminology, and to provide background on the SERDP and ESTCP programs and their current status.

The workshop started with presentations by the facilitator and by representatives of the DoD. These presentations provided background on the current status of cleanup efforts and the DoD-specific needs for improved technologies (Attachment C). The workshop then focused separately on the science and technology needs for both plume restoration and source remediation. Key research areas were identified in each of these areas, and problem statements were prepared for each research topic identified. Finally, each group (science and technology) voted separately on the highest priority topics. Because there was some overlap in these topics, these high-priority issues were then combined and segregated into three general focus areas.

The following sections discuss the science and technology needs that were identified, and the final summary presents the combined priority focus areas and the general conclusions resulting from the discussions. In addition, a section is included to identify some of the moderate-priority research areas.

3 Key Issues

Participants generally agreed on several key issues:

1) Research on source zones is a more pressing need at this point than research on plume restoration.

2) It is more important to improve our understanding and implementation of existing technologies than to develop new remediation technologies.

3) Our scientific understanding of source zones is inadequate, and better tools to evaluate the source architecture, total contaminant mass, and the rates and mechanisms of contaminant release from sources are needed.

4) It is important to better understand the processes occurring at the pore-scale, especially at the interfaces surrounding non-aqueous phase liquids (NAPL) in the subsurface.

5) *In situ* thermal and biological treatment technologies are the most critical areas for technology investments at this time.

One area in which there was not full agreement was the extent of source characterization that should be performed, and therefore the importance of more detailed characterization tools. Some argued that one can never know enough prior to starting source treatment, and pilot-scale treatment tests should be used as part of the characterization process. Others favored far more characterization in general, arguing that dollars spent on characterization generally result in far larger savings during the eventual remediation.

One interesting point raised was that DoD sources tend to be relatively unique. As opposed to many operating facilities, DoD sites often have dispersed source areas (such as disposal sites with poor historical records regarding locations of disposal), and the sources (e.g., leaking drums) are often numerous and sporadic in distribution. These features make source delineation and characterization particularly difficult for DoD's CAH sites.

Finally, technology transfer was repeatedly mentioned as a pressing need, and an area in which the SERDP/ESTCP programs could provide valuable assistance. Most participants felt that the DoD site cleanup process could be improved by a focused technology transfer effort involving the SERDP and ESTCP programs.

4 Highest Priority Needs For Science and Technology

The research and development needs identified by the science and technology groups were combined into general headings (see Table 1 below). The problem statements developed by the science group participants are provided in Attachment D. The problem statements formulated by the applied technology group participants are provided in Attachment E.

As noted above, there was overlap between the working groups in several areas. The areas for which there was overlap included:

1) Effects of Source Zone Treatment (Science) and Benefits of Partial Mass Removal from Sources (Technology)

2) Source Delineation and Characterization (Science) and Source Zone Characterization and Flux Analysis (Technology), and

3) Bioaugmentation (Science) and Source Zone Bioremediation and Bioaugmentation (Technology).

Accordingly, given the importance of these areas deemed by both working groups, they are considered as the "highest priority" research needs. Each is discussed below combining the problem statements prepared by the two groups.

4.1 Effects and Assessment of Source Zone Treatment

The irregular distribution of the entrapped and pooled NAPL in source zone areas, coupled with natural variations in hydraulic conductivity and capillary properties, makes complete mass removal virtually infeasible for most source zone treatment technologies. Thus, it is likely that a significant fraction of the contamination will still remain after treatment. This contaminant mass may reside in pools or lower permeability regions that are less accessible to groundwater flow. Due to this relative inaccessibility, it is possible that mass fluxes from the source zone will substantially decrease, even though considerable contaminant mass remains. On the other hand, various treatment technologies have the capacity to increase mass flux by spreading the contaminated zone (through NAPL mobilization) or by increasing the NAPL/aqueous interfacial area (through solubilization).

Unfortunately, little is known of the influence of source zone treatment on contaminant mass fluxes, composition, and source zone architecture. Such information is critical to the evaluation of potential risk reduction and the

cost/benefits of applying a particular remediation technology. Research should include examination of the fundamental processes influencing mass fluxes, the

TABLE 1

HIGH PRIORITY RESEARCH AND DEVELOPMENT NEEDS IDENTIFED DURING WORKSHOP

SCIENCE NEEDS

RESEARCH NEED		**RANKING**
HIGHEST PRIORITIES		
A.	Assessment of Source Zone Treatment Technologies	1
B.	Physical/Chemical/Biological Interactions at NAPL Interfaces	2
C.	Source Zone Delineation and Characterization	3
D.	Quantification of Uncertainty	4
E.	Effects of Treatment Amendments	5
F.	Cost Effective Assessment Tools and Methodologies	6
G.	Bioaugmentation	7
MODERATE PRIORITIES		
H.	Methods for Cost Comparisons	8
I.	Transport in Fractured Media and Karst Aquifers	9
J.	Behavior of Source Zones	10

TECHNOLOGY NEEDS

HIGHEST PRIORITIES		
A.	Benefits of Partial Mass Removal from Sources	1
B.	Source Zone Characterization and Flux Analysis	2
C.	Diagnostic Tools to Measure Performance	2
D.	Assessment of Thermal Treatment	2
E.	Source Zone Bioremediation and Bioaugmentation	3
F.	Sustainability of Monitored Natural Attenuation	4
MODERATE PRIORITIES		
G.	Improved Prediction of the Risks to Indoor Air from Soil Vapors	5
H.	Decision Trees for Source Delineation and Remediation	5
I.	Surface Water Discharge and Use of Engineered Wetlands	6
J.	Consistent Cost Comparisons for Different Treatment Technologies	6
K.	Treatment in Fractured Media	7
L.	Scale-up Issues (Pilot- to Field-Scale Transfer	8

development of predictive models, and the field assessment and monitoring of pre- and post- treatment mass fluxes, or "mass release rates". The mass release rate can also change as a function of time, so a key practical question is to understand how much reduction in time or institutional monitoring of the system can be achieved by a source removal activity.

Measuring contaminant mass release was identified as perhaps the most pressing technical challenge within this general area. In recent years, two methods have been used by researchers, although no approach has had significant commercial use. The first is to rely on measurements of contaminant concentration data from transects of wells (often multilevel wells). The second method is based on groundwater extraction using monitoring wells installed in transects across the plume. Both have advantages and limitations, and there is no consensus on the "best" approach for different situations. Research is therefore needed to develop and test these approaches, and possibly others, and then compare these alternative approaches under field conditions. Eventually, this work should result in guidelines for selecting and implementing the approach best-suited to specific plume and hydrogeologic conditions.

4.2 Source Zone Delineation and Characterization

This area includes the need for research and development of better tools to delineate source zones, and research that allows meaningful characterization of those sources. The delineation of sources is a long-term problem that makes any approach to assessing and remediating CAH-impacted groundwater extremely difficult. But even if one can fully define the boundaries of a source zone, remediation will be difficult unless one can also characterize its attributes in a meaningful way.

The physical and chemical attributes of source zones are currently difficult to evaluate, yet these features can have important influences on the feasibility, selection, design, and performance of remediation technologies. These attributes include both the macro-scale and local distributions of NAPL in the subsurface, as well as the chemical composition of the NAPL. The macro-scale distribution of NAPL defines the overall geometry of the source zone and is an important determinant of the total mass/volume of NAPL that is present. The local distribution of NAPL is equally important, because NAPL present in subregions of fine-grained material is less accessible to remediation agents than that present in subregions of coarse material, for example. The chemical composition of the NAPL, as determined by historic releases and subsequent weathering, affects interfacial tension, viscosity, density, wettability, and other interactions at the NAPL-mineral interfaces, as well as the potential for enhanced and natural biodegradation.

At present DNAPL source zones are identified by indirect means, primarily by inference from groundwater and soil concentration data. There are no accepted tools or test protocols available for the direct measurement of DNAPL composition and mass. There has been progress in developing and testing new approaches to DNAPL detection and quantification, such as partitioning tracer tests, use of radon abundance data, and geophysical surveys. These methods can be helpful in locating DNAPLs, and partitioning interwell tracer tests in particular have shown considerable promise for estimating the total DNAPL mass in some situations.

However, all of these methods have limitations restricting their widespread use for evaluating DNAPL composition and mass. Such composition and mass measurements require direct measurement analytical techniques, or assessment protocols involving several kinds of measurements. Research is needed to explore the potential for spectroscopic, wet chemical, optical or other techniques, singly or in combination, to provide data on the composition and abundance of DNAPL components from various kinds of DNAPL-contaminated soils.

4.3 Bioaugmentation

The argument for bioaugmentation rests on the observations that some sites do not appear to have the presence, or adequate numbers, of organisms capable of completing all of the steps required for reductive dechlorination of PCE or TCE. In many cases, the accumulation of cDCE has been observed, and in some cases, this accumulation appears to be relieved by the addition of appropriate organisms. Further, drastic source remediation technologies, such as *in situ* thermal treatment, may reduce the numbers of appropriate organisms, so that bioaugmentation may be helpful in treating the residual left after this first phase of treatment.

Although bioaugmentation with organisms capable of complete dechlorination to ethane (ETH) has resulted in complete conversion to ETH on site, this has not proven to be successful everywhere. In particular, little is known regarding the distribution of microorganisms from delivery points. Past work on adding organisms to the subsurface (generally with aerobic bacteria) has suggested that added organisms have difficulty moving through the aquifer or becoming established in a field environment. However, the limited data from field bioaugmentation studies using a dehalorespiring microbial culture suggest that these organisms appear to become established quickly and move readily through aquifer materials.

Currently, methods for applying bioaugmentation have been based on the judgment of the professionals involved. Although there have been apparent successes, the development of this technology will remain "casual" and irreproducible without careful studies of the factors influencing survival and effectiveness of the added organisms. Research is needed under a variety of

field conditions, and particularly in high-sulfate environments. Molecular (or other) tools are needed for the cost-effective monitoring of the fate and distribution of the introduced microbes. Research is also necessary to explore alternative delivery systems, as well as to develop quantitative models to predict subsurface transport of the organisms.

5 High Priority Needs for Science And Technology

In addition to the overlapping needs discussed in Section 4, several problem areas were identified as "high priority" areas by either the science or the technology working groups. Each of these problem areas is discussed in the following sections respective to the two working groups.

5.1 High Priority Needs for Science

The science group identified several other "high-priority" needs, which are discussed in the following sections. These needs include:

- Physical, Chemical, and Biological Interactions at NAPL Interfaces,
- Uncertainty Quantification, and
- Effects of Treatment Amendments

5.1.1 Physical, Chemical, and Biological Interactions at NAPL Interfaces

The interface between the NAPL and aqueous phase in the subsurface is a critical location where interactions can occur that can impact source zone treatment effectiveness. However, the nature, rate and extent of interactions that occur at the interface are poorly understood. For example, in theory, interphase mass transfer can be dramatically enhanced due to NAPL contaminant degradation reactions that occur in the aqueous phase. Such reactions can result in reducing the thickness of the boundary layer and increasing the concentration gradient across it, thereby increasing dissolution rates by factors of 10 or more.

Such enhancement effects assume that interfacial resistance does not develop as a result of the reactions (e.g., interfacial film formation due to reaction products from oxidation or microbial reactions). Or, treatment agents may be delivered that increase dissolution from the NAPL into the aqueous phase or preferentially partition to the NAPL-water interface, thereby enabling reactions to occur at that location which thereby enhance dissolution and degradation and source zone treatment effectiveness. Further research is needed on the fundamental processes controlling interactions at the interface including the effects of NAPL architecture and composition, aqueous phase water chemistry and microbiology, and flow regime characteristics.

5.1.2 Managing Uncertainty in Risk Assessment and Remediation

The selection, design, and evaluation of a remedial approach at a particular contaminated site are necessarily based upon imperfect knowledge of site characteristics and properties. The extent and distribution of the contaminant and the hydraulic/chemical/biological processes that control its migration and persistence in the subsurface are extremely difficult to quantify and assess. Furthermore, the significant heterogeneity of most subsurface environments dictates that critical site parameters, such as hydraulic conductivity, groundwater velocity, microbial activity, contaminant concentration, and sorption/desorption rates can vary over orders of magnitude, within relatively short spatial distances. This high degree of spatial variability in properties makes the complete characterization of a site an essentially unobtainable goal. Predictions or decisions needed for the remediation of an environmentally impacted site that are made based upon this knowledge, consequently, are subject to a relatively high degree of uncertainty.

Mathematical models are widely used in practice to synthesize our understanding of the physical/chemical/biological processes affecting contaminant behavior in the subsurface. Such models are indispensable tools for the assessment of risks associated with a contaminated site and for the evaluation of remedial alternatives or prediction of remedial performance. These mathematical models have generally been validated for small-scale experiments, in which the system properties are controlled or extremely well characterized. The meaningful application of such models in a natural field setting, however, is fraught with difficulty. For example, the processes incorporated in the model that controlled the contaminant behavior under the experimental model validation conditions may not be the processes operative at the field site. Thus, model predictions may be very inaccurate. Furthermore, application of a model requires that the user specify the initial site conditions and the spatial distribution of all subsurface properties. Since our knowledge of these conditions and properties is severely limited at most sites, these properties are typically assumed or estimated. Poor estimates will lead inevitably to inaccurate predictions. A further complication is that many field property measurements are obtained at a scale that is not directly transferable to the scale required by the model. Use of parameters measured at an inappropriate scale can result in additional inaccuracies in model predictions.

Despite the difficulties associated with site characterization and model application, as described above, contaminated site management ultimately requires the estimation of properties and the application of modeling tools for decision-making. Unfortunately, the level of uncertainty inherent in parameter estimation and model predictions is generally not recognized or expressed when these models are used. Meaningful risk assessment and cost/benefit analysis, however, are not possible without an understanding of uncertainty. Evaluating the uncertainty in model predictions is particularly essential in the

risk assessment associated with monitored natural attenuation and in post-treatment source zone mass flux reduction. Thus, there is an urgent need for the development of tools and methodologies to both quantify and reduce the uncertainty associated with parameter estimation and model predictions. Such tools could take the form of improved in situ characterization techniques for hydraulic, chemical, and biological processes/properties, improved statistical protocols for parameter estimation from sparse and variable quality data, improved methods for parameter scale-up, improved methods/models for assessing remedial performance uncertainty, or improved remedial designs/technologies that are relatively insensitive to spatial variability in subsurface properties. The development of these modeling protocols/tools will also be of great assistance in evaluating the need for additional site characterization work and in formulating optimal site characterization plans to reduce uncertainty. Additional research is also needed to demonstrate and validate parameter estimation methods, remedial performance simulators, and uncertainty modeling tools at the field-scale, using real site data.

5.1.3 Effects of Treatment Amendments

The *in situ* treatment of soil and groundwater contaminated by chlorinated solvents can have impacts on subsurface conditions. Potential effects that require further research and understanding include treatment-induced changes such as:

1) Alterations in site physical, chemical and microbiological parameters that impact flow and transport processes, and thereby affect contaminant behavior and treatability *in situ*.

2) Alterations in NAPL distribution and composition (e.g., due to solubilization and mobilization).

3) Geochemical and microbial perturbations.

4) Degradation of downgradient water quality.

For example, addition of chemical oxidants can cause production of gases or precipitates that may reduce permeability or limit the delivery and mixing of the reagents. Thermal treatment can cause migration of NAPL into previously unimpacted areas or alter the microbial community. Surfactants can potentially enhance subsequent biodegradation. Aggressive source remediation can impact downgradient water quality parameters, such as dissolved oxygen, concentrations of soluble metals, pH, and dissolved solids, and our ability to predict these changes is limited.

The potential for occurrence of these and related effects as well as their relative impacts (positive or negative) are highly dependent on the complex interactions between treatment process design and pretreatment environmental conditions. We do not currently have sufficient understanding or guidance

available to assist remedial project managers in adequately predicting or monitoring these potential side effects.

Questions that need to be addressed, in separate research projects, or as part of other pilot tests or technology demonstrations, include:

1) What is the biological diversity before remediation and how does it change as a result of remediation? This information is specifically needed in relation to the architecture of the NAPL in the formation.

2) What does the treatment system leave behind and how do residual materials continue to react both biologically and chemically in the system?

3) How does treatment impact the flow field? That is, does the treatment block the formation as a result of precipitation or plugging? Does treatment increase the effective permeability as a result of mass removal or mass destruction?

4) What hazards are associated with any byproducts produced as a result of treatment (e.g., metabolites from bioremediation or oxidation)?

5) How long does the system take to return to a point at which there is no environmental concern?

6) What are the potential impacts on water quality parameters downgradient of the treated area?

5.2 High Priority Needs for Technology

The technology group identified five high-priority needs, which are discussed separately in the following sections. The technology needs include:

- Diagnostic Tools to Evaluate Remediation Performance,
- Assessment of *In Situ* Thermal Treatment,
- Monitored Natural Attenuation,
- Source Zone Bioremediation, and
- Source Characterization Tools.

5.2.1 Diagnostic Tools to Evaluate Remediation Performance

The performance of existing and developing remediation technologies needs to be evaluated, both at the pilot scale and in field-scale implementations. For a number of remediation technologies, this evaluation may require developing

new diagnostic tools. It also requires better technical guidance on using diagnostic tools to improve the conceptual model of remediation performance. An example of this approach involving SERDP and ESTCP has been the development of technical guidance and diagnostic tools for *in situ* air sparging, which has helped this technology evolve from being a "hit and miss" approach to a more robust remediation tool.

The first step in this effort is to identify the technologies that need the development of additional tools. Table 2 represents an initial effort at identifying the existing tools and the need for new methods. The second step may be development of a conceptual framework for utilizing those tools to evaluate specific remediation technologies and the development of site-specific conceptual models of remediation performance. However, a related component is the integration of the diagnostic tools to provide meaningful comparisons between different technologies.

TABLE 2

DIAGNOSTIC TOOLS FOR REMEDIATION TECHNOLOGIES

Remediation Technology	Existing Diagnostic Tools	New Tools Needed?	Potential New Tools
Pump and Treat	Water levels, concentrations	No	
In Situ Air Sparging	Tracer tests, pressure, concentrations	No	
Chemical Flooding	Concentrations, push-pull tests, partitioning tracer tests	Not yet determined	
Thermal Treatment	Temperature	Not yet determined	
Biodegradation	Gene probes, concentration, daughter products	Yes	
Groundwater Circulation Wells/ Communicating Wells		Yes	Tracer tests
Permeable Reactive Barriers		Yes	Tracer tests, velocity probes
Enhanced *In Situ* Flushing		Not yet determined	

5.2.2 Assessment of *In Situ* Thermal Treatment

The current status of several "emerging" technologies for source treatment was reviewed (see Table 3 below). The clear consensus was that the emerging technology most in need of research was *in situ* thermal treatment. This evaluation reflected both the promise of the technology and the uncertainties regarding its implementation. Thermal treatment has the potential to remove a very large fraction of the source mass, and may be able to treat even the less permeable areas within the source zone (as opposed to technologies relying on hydraulic delivery of reagents). However, it is expensive and there have been few independent evaluations of the technology (i.e., most reports to date have been generated by the technology vendors).

The ability of thermal treatment to overcome the difficulties presented by large permeability contrasts *in situ*, as a result of thermal conduction into the low-permeability zones, needs to be demonstrated. This demonstration should include sites with large permeability contrasts. An important issue in the demonstration is how and when to sample the subsurface after a thermal treatment. Core samples collected while the subsurface is still hot cannot be relied upon for demonstration due to the high potential for volatility losses during sampling. A reliable sampling methodology therefore needs to be established in order to evaluate the effectiveness of thermal treatment.

TABLE 3

NEEDS FOR EMERGING SOURCE TREATMENT TECHNOLOGIES

Priority	Technology	Research and Development Needs
1.	Thermal	1. Independent Demonstrations 2. Low Temperature Phenomena 3. Permeability Contrast Areas
2.	Bioremediation	1. Understand Dissolution/Degradation Processes 2. Bioaugmentatsion Protocols & Regulatory Questions
3.	*In Situ* Chemical Oxidation	1. Proper Implementation 2. Critical Analysis
4.	*In Situ* Flushing	1. Benefits of Partial Mass Removal 2. Potential for Redistribution
5.	Electrochemical Treatment	
6.	*In Situ* Chemical Reduction	

Another significant research need is to evaluate the possibility of condensation of the NAPL at the edge of the heated zone. To allay concerns that the results reported by thermal remediation proponents may be biased, there is a need to reassess the performance of those successful projects by independent researchers, with a particular emphasis on locations at the edge of the heated region. The group was also intrigued by the number of *in situ* thermal treatment projects that have been initiated or completed. Approximately 70 projects have been identified, many of which were done at DoD sites (see Attachment F). A careful evaluation of the results from these pilot- and full-scale applications could be very helpful in assessing the technology and in identifying questions for future research and development. Finally, the group also identified the potential for effective treatment at relatively low temperatures (<100 F) as being worth further study.

5.2.3 Monitored Natural Attenuation

Monitored natural attenuation (MNA) has become widely used for petroleum sites, and is becoming more common for CAHs. There is little doubt that MNA will be used for many DoD sites, either after more aggressive treatment or in some cases as the sole remedy. It is economically attractive when it works, and further, MNA may be the only practical alternative for many plumes that are very large in size and/or extend under structures or developed built-up areas. However, there are significant questions regarding the conditions under which MNA can be used with confidence, particularly when the attenuation processes are relatively slow. The most critical need is to assess the long-term sustainability of MNA.

Reductive dechlorination is the most important attenuation process, and appears to be occurring at many sites. However, the process will have to continue to be effective over several decades in many cases, and such long-term performance requires a continual sufficient supply of electron donors and/or nutrients. There is little long-term data available to evaluate the long-term efficacy of MNA under different environmental conditions. Guidance on appropriate characterization methods and development of accurate predictive models are needed to increase our confidence in the use of MNA at a specific site.

In addition, many CAH plumes are under aerobic conditions, so that biological reductive dechlorination will not be a major natural attenuation process. However, other natural attenuation mechanisms may occur, including dilution, dispersion, sorption, volatilization, abiotic degradation, and aerobic biodegradation. These processes may occur at very slow rates, but still at rates that can be significant in the long term. An effective evaluation and assessment of these and other natural attenuation processes that might occur at these sites would provide the following benefits:

- Provide DoD with realistic expectations of what these mechanisms might be able to accomplish in the long term.
- Provide evidence that can be used to convince the regulators and the public that long-term natural attenuation is the best approach for these sites.

Laboratory studies may be required to investigate some of these mechanisms. Long-term field studies will also be required, to investigate the questions regarding the sustainability of MNA and the contribution of slow attenuation processes. Finally, models and measurements that integrate mass discharge and natural attenuation capacity are needed. MNA assessments can provide valuable guidance on the degree of source removal needed to ensure effective containment of the residual mass. However, we need a clear understanding of both the mass discharge that will occur after treatment, and the dissolved mass that can be reliably contained by MNA under given environmental conditions.

5.2.4 Source Zone Bioremediation

The second technology identified as needing more research and development work was *in situ* bioremediation of source zones. The questions regarding this technology included the needs for a better understanding of the interrelated dissolution and degradation processes, and for a better understanding of bioaugmentation. The latter need was addressed in Section 4. However, the first question is briefly discussed below.

Stimulating biodegradation in a DNAPL source zone can potentially be a very economical approach to CAH plume remediation. Calculations and laboratory evidence suggest that overall cleanup time can be reduced as much as 16-fold by stimulating biodegradation *in situ*, as opposed to relying on water flushing alone. However, many field-scale phenomena could significantly reduce the potential benefits of *in situ* bioremediation, and the controlled field-scale studies needed to evaluate the technology are not available.

Such studies will be difficult, however, because the impacts of biodegradation are complex. Microorganisms can degrade CAHs near, if not at, the DNAPL/water interface. That interfacial biodegradation can increase the release of contaminants from the NAPL phase. Microbes can also directly enhance dissolution through production of biosurfactants or other metabolites. The released CAHs may then be degraded in the dissolved phase or migrate to monitoring or extraction wells. Further, biodegradation of the source can alter the chemical composition of CAHs in the NAPL and surrounding dissolved phase, changing the potential for dissolution and biodegradation. The rates of dissolution and degradation will also likely change significantly over time. Finally, accurate measurement of the impacts on source mass and environmental risk is difficult, for reasons already discussed (e.g., Section 4.1).

Obviously, careful long-term studies under field conditions are essential for demonstrating this technology. Mass balances to fully understand the effects on mass reduction, enhanced dissolution, and overall biodegradation will be difficult to perform. But more mechanistic research is also needed to better understand the interrelated dissolution and degradation processes. Without a more thorough understanding of these complex interrelated phenomena, any predictions regarding the economic or environmental benefits of using this approach will be suspect.

5.2.5 Source Characterization Tools

In addition to the discussion of source zone characterization given in Section 4.3, the technology group identified two other relatively specific tools that need to be developed. The two are related, and both could in fact be part of a two-phased approach to source characterization. The first need is for “variable-scale source delineation techniques.” This term is intended to describe source delineation methods that can integrate information needed for identifying source zones over moderate scales (on the order of a few meters to tens of meters, for example).

DNAPL migration and distribution in the subsurface is greatly affected by heterogeneities at many different scales. Typically, point-scale techniques (i.e., wells or borings) have been used to locate DNAPL source zones. However, detailed delineation can require many points, often at great expense, and the method can often be literally “hit or miss”, especially with the types of source areas common at DoD sites (i.e., large areas with sporadic sources). For these situations, something larger than point-scale delineation techniques would be helpful.

Historically, it was hoped that geophysical methods could be used at larger scales to help delineate DNAPL sources. However, these methods have proven unsuccessful. For recent releases, soil vapor sampling is helpful for locating potential source areas by indicating the migration pathway through the vadose zone. An analogous methodology is desirable for the saturated zone. One example of such an approach might be push-pull tests of various types. In general, economical approaches are needed that can be employed relatively rapidly and inexpensively to allow multiple investigations at various locations at a given site (as may be necessary at many DoD sites). The technology must yield convincing evidence of DNAPL presence, have a very low rate of “false positives”, and have a reasonably low “detection limit.”

The second need is for improved methods to estimate total contaminant mass in a source zone. Specifically, more economical and/or rapid approaches for determining contaminant concentration distributions via profiling approaches (discrete or continuous measurements) would be helpful. The goal of such a tool would be to reduce costs to the point that it is feasible to conduct a large number of such profiles, thus reducing uncertainty in contaminant distribution (and errors associated with interpolation between sampled points). Many DoD

sites have patchy distributions of DNAPL contamination (hotspots) over rather large areas, so such technologies could be employed in a two-phased approach involving:

1) Cross-gradient transects to identify the location of high concentration "cores" within the plume width (upgradient of which should be the portions of the subsurface that are most contaminated by DNAPL, i.e. hotspots); and

2) Areal applications to hone in on and characterize hotspots.

Note that the first technology need identified (variable-scale source delineation) could conceivably be applied as the second phase of the two-phase approach outlined above.

6 Moderate Priority Needs for Science and Technology

There were a number of problem areas identified in both the science and technology working groups that, although considered important, were not deemed as "high priority" areas. These moderate priority areas have been combined to exclude overlapping areas below:

- Transport and Treatment in Fractured Media and Karst Aquifers
- Methods for Consistent Cost Comparisons
- Improved Prediction of the Risks to Indoor Air from Soil Vapors
- Decision Trees for Source Delineation and Remediation
- Surface Water Discharge and Use of Engineered Wetlands
- Scale-up Issues (Pilot- to Field-Scale Transfer)

The first four of these "moderate" priority research needs are discussed in the following sections. Further descriptions of these needs are provided in Attachments D and E.

6.1 Fractured Media

Both groups addressed the need for better understanding of fractured media, because many DoD sites are located in areas where DNAPL has migrated into fractures (e.g., sites located over fractured bedrock, clays, or karst topography). Assessment and remediation of such sites are extremely difficult challenges.

In fractured media, most of the permeability is associated with the fracture system while most of the storage is associated with the block matrix. Separate phase chlorinated solvents will preferentially move through and become trapped within the fracture system. Trapped NAPLs will rapidly dissolve into the matrix system, from which they will slowly diffuse back to the fracture system for transport. Treatment of CAHs in fractured media is often not considered because of concerns that aggressive treatment will cause further downward migration, although there is little data on this potential problem. Characterization and remediation of karst systems is particularly difficult because of the extreme variability between different karst systems.

Specific research needs in this area include:

1) New techniques for identifying the primary flow paths and their relation to the location of the NAPL;

2) Methods to enhance diffusion of reactants (e.g., oxidants or surfactants) into the matrix;

3) Development of techniques (such as co-injection of air) that eliminate the potential of NAPL accumulation and mobilization in fractures during treatment (particularly critical for thermal treatment); and

4) Tools to evaluate transport within fractured media.

6.2 Cost Comparison Methods

Both groups also identified the need for consistent and accurate cost comparisons. In particular, participants felt that technologies should compare costs with pump-and-treat systems, since this technology is the “benchmark” and has a long history of actual cost data. Participants also felt that in many cases, the cost comparisons developed by vendors or researchers are incomplete and inaccurate, if not misleading. Guidance on developing accurate cost comparisons would be very helpful in ensuring that technologies are compared fairly. Possible approaches include developing typical scenarios to represent the range of DoD sites, and cost templates with consistent labor and material rates.

6.3 Improved Vapor-to-Indoor Air Predictions

At many sites, the migration of vapors through soil to indoor air is often a significant risk driver for groundwater impacted by CAHs. This potential pathway of migration is gaining increasing attention from the EPA and state regulators. However, there are significant uncertainties in our current predictive models and evaluating this pathway is often technically and politically difficult. In addition, the needed monitoring programs and engineering controls to prevent exposures can be very expensive.

The research effort may include:

1) Additional field studies at a variety of sites to understand the conditions at which vapor to indoor air may be a significant risk pathway;

2) Upgrading of the currently-used models to make them more realistic, using data from real-world DoD sites for calibration; and

3) Technical transfer of the information that is available to the RPMs and their consultants.

This work should be coordinated with related efforts by other parties (such as EPA, specific states, industry groups or specific branches of DoD.

6.4 Decision Trees for Source Characterization and Remediation

The technology group believed there was a need for guidance in the decision-making process involved in addressing source zones. This process is complex and influenced by a large number of factors, including technical, economic and political issues. A conceptual framework for determining how to approach source characterization and remediation could provide needed guidance and consistency. This conceptual model might take several forms, including a decision tree or an expert system, for example. Such a decision tree must be both robust (capturing the potentially wide range of processes involved), as well as current (maintained regularly in order to keep up with the rapid changes in this area).

7 Conclusions and Recommendations

The high-priority research needs were combined and organized under three general headings, corresponding to historic SERDP/ESTCP thrust areas:

1) Environmental Processes Research
   - Physical/Chemical/Biological Processes at NAPL Interfaces
2) Performance Assessment and Risk Analysis
   - Source Zone Delineation and Characterization
   - Benefits of Partial Mass Removal
   - Uncertainty Quantification
   - Impacts of Treatment Technologies
   - Diagnostic Tools
3) Remediation Technologies Development
   - Thermal Treatment Evaluation
   - Source Zone Bioremediation
   - Bioaugmentation
   - Sustainability of MNA

These priorities are directly related to the key conclusions and general recommendations that resulted from the workshop discussions. These recommendations for future SERDP and ESTCP research and development work are discussed in the following sections.

7.1 Recommendation #1: Focus on Source Zone Treatment

One of the more important conclusions was that research and development of source treatment technologies were considered far more important at this stage than improved plume treatment. This emphasis has resulted from the fact that plume remediation technologies are at a more mature stage. In addition, recent development of more aggressive source-zone treatment technologies has caused a reevaluation of the conventional wisdom that source removal is

"technically impracticable" and long-term containment will be the most common remedial strategy. As a result, there is increasing regulatory and public pressure to remediate source zones, despite significant scientific uncertainties about the value of source zone remediation, or even the appropriate methods to measure or define the "success" of such efforts. With limited resources, this area clearly has to be the focus of research and development efforts in the near future.

7.2 Recommendation #2: Develop Better Performance Assessment Tools

There was a clear overall priority for research in the general area of performance assessment. Even for the remedial technologies, the biggest questions addressed the need for assessing performance. The consensus was that it is more important to focus on optimizing existing technologies than to develop newer technologies. Several technologies are available, but we do not understand how well they work, especially under different site conditions, or how they can be optimized. In some cases, the tools needed to measure performance are inadequate. The development of better diagnostic tools, and guidance on the use of existing tools, are critical needs.

7.3 Recommendation #3: Develop Tools to Measure Mass and Mass Release Rates

Better tools and techniques are needed to estimate both the total contaminant mass in source zones, and the mass release rates from those sources. To measure the impacts of source treatment, or to understand the real risks posed by a residual source, it is essential to have accurate estimates of the total mass and the mass release before and after treatment. Combining mass release rates with estimates of natural attenuation capacity or fate and transport models can allow us to develop meaningful risk-based plume management strategies and regulatory approaches. However, the current state of the science is not adequate for these needs. As a result, we cannot determine the "success" of source removal efforts, or set reasonable performance goals for such efforts, or even evaluate the need for source removal at all.

7.4 Recommendation #4: Focus on Existing Remedial Technologies

At this point in the evolution of our approaches to CAH sites, better use of existing technologies will be more valuable than the development of still newer technologies. Participants clearly supported the preparation of better "state of the art" technology assessments (i.e., reviews of past and ongoing pilot- and full-scale applications), and the development of improved diagnostic tools and guidelines to optimize the performance of existing technologies. The field has matured to the point that the basic remedial

options have been developed and improvements will come from better implementation of existing approaches.

7.5 Recommendation #5: Focus on Thermal and Bioremediation Technologies

In terms of specific remedial technologies, thermal treatment was considered the most promising area for future investments of research funding. This conclusion reflected both the potential for *in situ* thermal treatment, and the current state of its development. The other major priority for technology demonstration and development was *in situ* bioremediation, in several forms ranging from MNA to biostimulation of source zones, to the increasing use of bioaugmentation. This emphasis reflects the potential cost savings that can be realized through using passive or active bioremediation approaches. Further, both MNA and enhanced bioremediation were considered important because they are likely to be part of treatment trains for source zone remediation, in many cases following more aggressive technologies.

7.6 Recommendation #6: Evaluate Available Existing Data

Several participants felt that there was a wealth of data available to SERDP/ESTCP from DoD pilot- and full-scale remediation work that could provide valuable insights. This type of effort could be a first step in other programs (similar to the approach taken for *in situ* chemical oxidation). Alternatively, there are possible stand-alone efforts that could be helpful using this approach.

Specific suggestions for such “data mining” included: 1) Reviewing existing applications of *in situ* thermal treatment (discussed briefly in Section 5.2.2); 2) Reviewing other source zone treatment technologies, such as flushing or in-situ oxidation; 3) Reviewing any available data on the impacts of source treatment on dissolved plumes; and 4) Evaluating long-term plume dynamics (i.e., assessments of plume data from DoD sites with 10 or more years of data, to evaluate plume dynamics over that time and identify the factors that influence migration and stability).

7.7 Recommendation #7: Increase Technology Transfer Efforts

Finally, there was a clear recommendation for increased efforts in technology transfer. Specifically, participants encouraged SERDP/ESTCP to initiate a program to develop and conduct training courses targeting the DoD remediation project managers and their regulators. Such training should address the complexity of CAH plumes architecture and dynamics, and the tools available for characterizing and remediating CAH-impacted sites.

Attachment A

AGENDA

(revised 8/1/01)

WORKSHOP ON CHLORINATED SOLVENT REMEDIATION

Day 1 – August 6, 2001

Time	
8:00 – 8:15	Opening Remarks & Welcome: *Bradley Smith and Jeffrey Marqusee*
8:15 – 8:30	Workshop Objectives (*Michael Kavanaugh)*
8:30 – 8:55	DoD Cleanup Problem: Macroview *(Laura Yeh)*
8:55 – 9:20	DoD Operational Issues: Field perspective *(Johnnie Shockley)*
9:20 – 9:30	Q&A/ Discussion *(Michael Kavanaugh)*
9:30 - 10:00	SERDP/ESTCP Technology Investments: *Cathy Vogel*
10:00– 10:15	*Break*
10:15 – 10:45	Plenary group discussion on questions related to plume remediation & assignment of participants to breakout groups (*Michael Kavanaugh):* - *Do we understand the processes ?* - *Can we engineer the systems ?* - *Are there any (emerging) areas in which SERDP and/or ESTCP should invest; what R&D areas are 'done' ?*
10:45 – 12:00	Plume remediation breakout sessions: Science issues – *Herb Ward, Chair* Engineering issues – *Hans Stroo, Chair*
12:00 – 13:00	*Lunch*
13:00 – 14:00	Continue Plume remediation breakout sessions: Science issues – *Herb Ward, Chair* Engineering issues – *Hans Stroo, Chair*
14:00 – 14:15	*Break*
14:15 - 14:35	Plenary reconvenes; Summary outbrief from each plume breakout group Chair *(Ward, Stroo; 10 mins each)*
14:35– 15:05	Plenary group discussion on source zone issues and assignment of participants to breakout groups *(Michael Kavanaugh)* - *Do we understand the processes ?* - *Can we engineer the systems ?* - *What are the areas in which SERDP should invest; ESTCP ?*
15:05 – 17:00	Source Zone Remediation breakout sessions Science issues – *Herb Ward, Chair* Engineering issues – *Hans Stroo, Chair*
17:00 - 19:00	Free Time
19:00 – 20:00	*Dinner*

Day 2 – August 7, 2001

8:00 – 8:30	Plenary (*Mike Kavanaugh*): Day 1 update from each source zone breakout group Chair *(Ward, Stroo, 10 mins each)*
8:30 – 9:00	Plenary group discussion on source zone issues (*Mike Kavanaugh)* - *Priority areas for Day 2 breakouts*
9:00 – 10:00	Continue Source Zone Remediation breakout sessions Science issues – *Herb Ward, Chair* Engineering issues – *Hans Stroo, Chair*
10:00 – 10:15	*Break*
10:15 – 12:00	Continue Source Zone Remediation breakout sessions Science issues – *Herb Ward, Chair* Engineering issues – *Hans Stroo, Chair*
12:00 – 13:00	*Lunch*
13:00 – 13:40	Plenary (*Michael Kavanaugh*): Outbrief from each source zone breakout group Chair (*Ward, Stroo, 20 mins each)*
13:40 – 14:30	Wrap-up plenary group discussion on **science** issues for plume and source zone remediation *(Mike Kavanaugh)*: - *Prioritized investment areas for SERDP and ESTCP*
14:30 – 14:45	*Break*
14:45 – 15:45	Wrap-up plenary group discussion on **engineering** issues for plume and source zone remediation *(Michael Kavanaugh)* - *Prioritized investment areas for SERDP and ESTCP*
15:45 – 16:00	Concluding Remarks *(Michael Kavanaugh; Bradley Smith and Jeffrey Marqusee)*

Attachment B

Chlorinated Solvent Expert Panel Workshop
August 6-7, 2001

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Attachment C

SERDP/ESTCP CHLORINATED SOLVENTS WORKSHOP
BACKGROUND AND OBJECTIVES

1.0 INTRODUCTION

The Strategic Environmental Research and Development Program (SERDP) and Environmental Security Technology Certification Program (ESTCP) are Department of Defense (DoD) programs designed to foster research and technology development needed to help DoD perform its mission. These programs are executed in full partnership with the Department of Energy and the Environmental Protection Agency (EPA).

Environmental cleanup is one of the major thrust areas in the SERDP/ESTCP programs (the others are pollution prevention, compliance, conservation, and unexploded ordnance). Although DoD facilities have numerous types of contaminants, chlorinated solvents are by far the most prevalent, particularly the chlorinated ethenes such as trichloroethylene (TCE) and perchloroethylene (PCE), but related compounds such as trichloroethane (TCA), vinyl chloride (VC), dichloroethenes (DCE), and carbon tetrachloride (CT) also represent significant concerns. These chlorinated aliphatic hydrocarbons (CAHs) also remain among the most difficult to remediate, despite several years of research and development.

SERDP is a more basic research program aimed at the development and application of innovative environmental technologies that will reduce the costs, environmental risks, and/or the time required to resolve environmental problems while simultaneously enhancing safety and health. SERDP funding levels are approximately $55 Million annually, with the environmental cleanup thrust area representing slightly under 30% of the total funding.

ESTCP is a more applied program that seeks to promote innovative, cost-effective environmental technologies through demonstration and validation at DoD sites. The current ESTCP funding is approximately $20 Million annually, with the cleanup thrust area representing almost 50% of the total. Chlorinated solvent research represents only one area of the overall cleanup program (other areas include unexploded ordnance, metals and other compounds such as perchlorate and MTBE). Further information on these programs is available on the program web sites, at http://www.serdp.org/ and http://www.estcp.org.

The SERDP and ESTCP programs have reached a point at which it is necessary to refine and redefine their overall strategic plans. The following sections discuss the objectives for this workshop, and provide background on the programs, as well as a brief overview of the technical issues affecting the cleanup of CAH sites. Finally, the document presents an initial list of the questions the workshop is intended to address. This document is not intended to be an exhaustive discussion of the topic, but an introduction and starting point for the workshop.

1.1 Workshop Objectives

This workshop is intended to develop a strategic plan to guide research and technology development in the next 5-10 years, specifically in the area of cleanup of sites with groundwater contaminated by chlorinated solvents. The overarching question is how these programs can best invest their limited research, development, and demonstration funds to improve DoD's ability to effectively address its chlorinated solvent contamination sites. The plan should recognize DoD's unique mission needs, as well as the technical and economic problems faced at all sites with chlorinated solvent contamination of groundwater.

This workshop should identify the major basic and applied research needs, the specific technical issues that must be addressed to meet regulatory and other stakeholder concerns, and the major gaps in our scientific understanding of CAH contamination and cleanup. Further, the workshop should prioritize these research needs and identify those areas with the greatest promise to help DoD accomplish its goals.

2.0 BACKGROUND

SERDP and ESTCP have sponsored numerous projects aimed at improving our ability to cost-effectively remediate groundwater contaminated with CAHs. The current SERDP and ESTCP projects in this area are briefly discussed below. In the past, there has been considerable work in enhanced bioremediation of dissolved plumes, and somewhat less work in abiotic remediation methods. Recent work has focused on improved mixing in the subsurface and a better understanding of the effectiveness of source treatment technologies.

2.1 History

This history of SERDP and ESTCP research has to some extent mirrored the evolution of our plume management strategies in general. Until recently, the general approach was to use pump-and-treat approaches to contain, and attempt cleanup, of impacted groundwater. For example, EPA (1997) reported that pump-and-treat had been selected for groundwater treatment at 98% of over 600 Superfund sites, and chlorinated solvents are present at approximately 80% of all Superfund sites with groundwater contamination.

While containment is achievable, experience and greater scientific understanding over the last 20 years has led to a widespread recognition of the "technical impracticability" of cleaning up such plumes by pump-and-treat. Cleanup is particularly difficult when residual sources of dense nonaqueous phase liquids (DNAPLs) remain in the subsurface. For example, a survey of 77 sites undergoing pump-and-treat remediation showed that only eight had achieved cleanup goals, but none of the CAH sites surveyed had achieved cleanup goals (NRC, 1994 –Alternatives for Groundwater Cleanup).

During the 1990's, plume management strategies began to explicitly emphasize containment as the primary goal, and research and development therefore began to focus on less costly containment technologies than hydraulic capture with aboveground treatment. These technologies have included a wide range of *in situ* bioremediation approaches, primarily based on either anaerobic or cometabolic metabolism, abiotic technologies (notably zero-valent iron walls), and engineering approaches to overcoming

the difficulties of attempting remediation in the subsurface (such as funnel-and-gate, or various approaches to increasing subsurface mixing).

In the last few years, there has been increasing interest in a more aggressive strategy towards source removal. Newer technologies have been developed and marketed to overcome the perceived technical impracticabililty of source treatment. These technologies have included in situ oxidation, various *in situ* thermal technologies, surfactant and cosolvent flushing and bioremediation of DNAPL sources.

Evaluating these technologies for specific site applications has proven difficult. The initial capital costs can be very high, and the long-term efficacy and economic return are difficult to predict. As a result, both programs have increased their efforts in the area of source zone treatment. In addition, testing source removal technologies has proven very difficult because DNAPL source zones are often very difficult to characterize in the field, and aggressive technologies can cause pronounced changes in the distribution and nature of the remaining DNAPL.

2.2 DoD Needs

The DoD has many of the same issues as any responsible party, but there are some specific needs that should be realized. DoD owns or is responsible for an enormous area of property, in the United States as well as around the world. The number of sites potentially requiring cleanup has been estimated at approximately 17,000, and many of these are very large sites. The total DoD cleanup costs have been estimated at over $35 Billion (the total estimate for DoD and DOE is over $200 Billion).

Chlorinated solvents are by far the most prevalent groundwater contaminant, resulting from their widespread use. A recent estimate is that DoD owns over 3,000 sites contaminated with chlorinated hydrocarbons in the U.S. alone (EPA, 1997). The DoD has had to use their limited research funds to address other high-profile contaminants in recent years (notably MTBE and perchlorate), but chlorinated solvent contamination is still the single most pressing problem, and the need for more effective and less costly solutions remains.

Most of the potential sites have been investigated and remediation has been started at many. The typical approach has been to install pump-and-treat systems, and the operations and maintenance (O&M) of these systems has become a large, and growing, fraction of the total environmental expenditures. Further, at many of these sites, the remediation systems are removaing only a small amount of the mass of contaminants, and the rate of cleanup, and there is no end in sight to the continuation of the O&M costs.

For example, the Navy's NORM database lists 432 sites with groundwater CAH contamination. The NORM database indicates that 102 of these sites (roughly 25%) have been extracting and treating groundwater for over 10 years with little decrease in the CAH concentrations. However, although no sites have been identified that have achieved remediation endpoints, several have exhibited steadily decreasing concentrations and/or substantial decreases in mass. Clearly, at least some sites with DNAPL contamination have proven extremely difficult to remediate.

One option for these sites is to invoke a regulatory decision that it is technically impracticable to achieve site-specific cleanup levels. In some cases, this mechanisms allows the site to leave some contaminantion in place, and to rely on less aggressive technologies for groundwater remediation, such as monitored natural attenuation. On the other hand, the DoD has many properties that need to be closed and transferred to other entities, preferably without long-term environmental liability, long-term monitoring or the need for future aggressive remediation. For example, Congress has ordered the closure of many bases that could be redeveloped, and the properties will be worth far more without such continuing liability. If aggressive source treatment was feasible and appropriate, it would be far less costly to do such remediation before any property transfer and/or redevelopment.

DoD also has many active sites with a wide range of continuing operations. As a result, highly aggressive technologies such as *in situ* thermal treatment may be compatible with some site uses, but certainly not with all current operations. Health and safety considerations are extremely important in many cases. For example, recent highly-visible incidents involving the use of *in situ* oxidation have emphasized the need for clear operating procedures and a thorough understanding of the technology in order to prevent accidents.

DoD also typically has a high turnover in remediation managers. Site managers are often young and relatively inexperienced and are often assigned to environmental duties for short durations. Clear, user-friendly tools and guidance are therefore required, and innovative approaches can be slow to be accepted in some cases, or they can be indiscriminately implemented in others.

In addition, at many DOD sites, a community action group has been established, such as the Restoration Advisory Boards (RAB). These typically consist of local citizens directly or indirectly impacted by site related contamination. The RABs typically have a significant impact on remedial action decisions at DOD sites, and their concerns must be integrated into the cleanup strategy for the site. Often, the RABs are very resistant to use of less aggressive cleanup technologies or to reliance on MNA for site cleanup. These concerns have a direct impact on setting R&D priorities within the DOD for technology development.

2.3 Current SERDP Projects

Currently, SERDP's cleanup projects address three focus areas:

1) Improved Site Characterization and Monitoring
2) Remediation Technologies
3) Risk Assessment Methodologies

The need for improved site characterization and monitoring methods has been a consistent focus for several years. Our ability to detect and characterize contamination in the subsurface, particularly at sites with DNAPLs, has long been considered a major impediment to the design and implementation of cost-effective remedial strategies. Site investigations are expensive, and often we must install too many borings and monitoring wells, and the placement is far from ideal. The distribution and total mass of DNAPLs is

extremely difficult to determine, and the total flux of contaminants from these sources is also difficult to assess. Significant overall cost reductions would be possible if investigations and long-term monitoring could be done with less costly and more precise tools and techniques.

More cost-effective remediation technologies have also been a long-term focus area. As noted earlier, these projects tended to target less expensive dissolved plume containment technologies in the earlier years. In recent years there has been a growing interest in source removal and *in situ* destruction technologies, such as *in situ* oxidation, bioremediation of DNAPL sources, *in situ* thermal treatment and various flushing technologies. This gradual shift in interest has been driven by the potential for such technologies to help achieve closure of difficult sites, as well as to reduce the total life-cycle costs for remediation.

The focus on developing improved risk assessment methodologies is a more recent focus area. In particular, the effort to develop data and protocols for establish and support environmentally acceptable endpoints has been identified as a need. Work in this area has so far been limited to energetics and metals.

In addition to specific targeted projects, SERDP currently operates three National Environmental Technology Testing Sites, at Dover AFB, McLellan AFB and at Port Hueneme. The infrastructure, support, and site characterizations developed at these NETTS sites have fostered numerous development and testing projects by DoD and others.

2.4 Current ESTCP Projects

The current ESTCP cleanup program priorities are listed as:

- *In Situ* Treatment and Containment
- Rapid On-Site Characterization Technologies

The ESTCP cleanup thrust area has funded several projects designed to demonstrate and validate technologies that would treat dissolved phase CAH plumes. Driven by the need for *in situ* technologies that would provide less costly containment than pump-and-treat, many of the projects have focused on bioremediation, including both enhanced anaerobic approaches and cometabolic aerobic technologies. In addition, *in situ* air sparging has received considerable funding, for both CAHs and other volatile compounds.

Recently, the potential for abiotic technologies has received funding. These technologies include permeable reactive barriers, injectable cametal catalysts, electrokinetics and *in situ* chemical oxidation. Another recent focus has been source-zone treatments, including dynamic underground stripping, flushing with surfactants and cosolvents, and bioremediation using selected cultures. A listing of specific project titles is attached.

3.0 TECHNICAL OVERVIEW

The following brief review of the technical issues is not intended to be complete but to provide a common basis for discussions. This overview serves as an introduction to an initial list of the issues and questions for the Expert Panel.

3.1 Characterization

Location and characterization of DNAPLs is a major issue. Site investigations may typically locate less than 10% of the total DNAPL mass. Even in controlled release tests such as those done at Dover Air Force Base, accurate assessments of the initial and final mass of DNAPL are difficult.

The difficulties in characterizing source zones in particular stem from the complex source zone architecture that develops as DNAPLs migrate through the subsurface. The complex geometry and patterns of release from different sources (e.g., dissolution from saturated pools, dissolution from residual or trapped DNAPL, or diffusion from low-permeability areas) lead to initially complex dissolved phase plumes. This complexity, and the evolution of our understanding, has also led to confusion regarding terminology. Figure 1 illustrates typical features of the source zone architecture, and defines the major terms we intend to use in this paper and in the workshop discuussions.

Despite considerable research and development effort in the area, each characterization technique has its inherent limitations, and there is no clear guidance for which approach is best for given site conditions. Further, the difficulties posed by sites with DNAPL present make it unlikely that we will make significant improvements in characterization techniques over the next 5 years.

Partitioning interwell tracer tests have shown promise in characterization of the DNAPL mass and locations at several sites (Jin et al., 1995). Natural radon abundance has also recently been used to characterize DNAPL accumulations in the subsurface (Semprini et al., 1993).

Other techniques tested include ground penetrating radar, cross-well radar, electrical resistance tomography, 3-D seismic reflection, and electromagnetic resistivity (EPA, 1998). In addition, there are sensors deployed on cone penetrometers that can aid in locating DNAPL accumulations. Despite this effort and technological advances, characterization of DNAPL sites remains a difficult hurdle and a fundamental constraint to our ability to clean up such sites.

Several other "characterization" issues are discussed in other sections. Measuring matrix diffusion, mass flux, and natural attenuation capacity are all difficult problems that impact CAH site cleanups. Better understanding of the fate and transport of CAHs may affect risk-based decisions regarding site management. Finally, the human and ecological risks posed by CAHs may require more research.

3.2 Plume Remediation

The initial response to chlorinated solvent sites was almost uniformly to install pump-and-treat systems. DoD currently has hundreds of pump-and-treat systems in operation, with an ever-increasing annual cost for operations and maintenance. Following the general recognition that pump-and-treat was often ineffective for remediation of sites with residual DNAPL sources, and generally functioned as a costly containment strategy

(EPA, 1996; NRC, 1994), there has been considerable research and development on less costly containment approaches.

In recent years, less costly containment options have been developed (NRC, 1999). This area of research has been a primary focus of the SERDP and ESTCP cleanup program for many years, and it is important to consider the progress to date and the areas where research is still needed. The primary technologies used or in development are listed below:

<u>Physical Containment:</u>

1. Physical Barriers (e.g. Slurry Walls)
2. *In Situ* Vitrification

<u>*In Situ* Destruction:</u>

1. *In Situ* Anaerobic Bioremediation (Numerous Electron Donors)
2. *In Situ* Cometabolic Bioremediation (Phenol or Toluene)
3. In Well Catalysis
4. Permeable Reactive Barriers (esp. Zero-Valent Iron Walls)
5. *In Situ* Chemical Treatment
6. Monitored Natural Attenuation

<u>Removal</u>:

1. *In Situ* Air Sparging
2. Phytoremediation (May involve destruction)
3. Pump-and-Treat (May involve aboveground destruction or phase transfer)

In situ bioremediation has been extensively studied and is being implemented at many sites. Anaerobic biodegradation is the most commonly used approach because PCE in particular can only be degraded anaerobically (McCarty, 1997). Fundamental research on the microbiology has shown that several types of organisms can be involved, and redox status, the nature and concentrations of electron donors, and hydrogen availability are key control parameters (Becvar et al., 1997). Apparently a limited number of organisms are capable of complete dechlorination to ethane, and these may not be ubiquitous (Fennell et al., 2001).

A recent area of concern has been the observations that cis-DCE and vinyl chloride can accumulate in some plumes because they may be degraded much more slowly than the parent compounds. Reasons for this accumulation are not known and the mechanisms for c-DCE and VC removal are not clear (e.g., Bradley and Chapelle, 1997). The mechanisms for DCE and VC biodegradation are currently being studied intensively in SERDP funded efforts with Drs. Jim Tiedje, Alfred Spormann, Jim Gossett and Jim Spain. Because some sites may lack appropriate organisms at sufficient numbers, bioaugmentation has been increasingly proposed as being needed at sites. SERDP and ESTCP are funding some work to test this approach for source and plume remediation.

Current applied research and development has focused on the optimal methods to supply electron donors. Organic acids (Becvar, et al., 1997), slow-release lactic acid (Koenigsberg

and Sandefur, 1999), vegetable oil, molasses, and hydrogen gas (Newell et al., 1998) have all been used, but the relative strengths and limitations of these approaches are not clear. Methods to improve the delivery and distribution of electron donors in the subsurface may also need improvement.

Aerobic cometabolism of TCE and derivatives has been known for several years. A wide variety of cometabolites can support TCE biodegradation, and propane (Semprini, 1997), methane (Hazen et al., 1995), phenol, and toluene (McCarty et al., 1998) have been used in field demonstrations. Again, optimal methods to supply and distribute adequate oxygen and the cometabolites in the subsurface are of concern. In fact, the difficulties of controlling cometabolic reactions *in situ* are probably greater than for anaerobic bioremedation.

Phytoremediation has received recent attention, not only because plant uptake can be used for hydraulic control of impacted plumes, but because some plants can also absorb and metabolize chlorinated solvents from impacted groundwater (Schnoor, 1997; Newman et al., 1997). Further, some plants can enhance chlorinated solvent biodegradation in the rhizosphere as well (Chapelle, 1997). Phytoremediation has limited usefulness because of restrictions related to depth and climate.

Permeable reactive barriers have become widely used. The most common is the use of zero-valent iron (Gillham and O'Hannesin, 1994). Other types of barriers have also been investigated, including other metals, chemical oxidants, and sequenced and physical/chemical/biological systems (Fiorenza et al., 2000). Capital costs can be high, especially for deeper plumes, but operations and maintenance should be relatively low. There are, however, concerns over the potential for short-circuiting and fouling, as well as the actual longevity of PRBs under field conditions.

Other abiotic technologies are also being evaluated. For example, in a recent SERDP-funded project, palladium catalysts placed within wells are being tested (McNab et al., 2000). In situ air sparging has been tested at several sites for plume control, with mixed results (Bass and Brown, 1996). In situ chemical treatment, using a variety of oxidants and reductants, has been applied at many sites for plume treatment as well as source removal (Yin and Allen, 1999).

The difficulties posed by *in situ* treatment of chlorinated solvents have also led to research on methods to improve treatment technologies. Notably, mixing technologies have received recent attention. Groundwater communicating wells and recirculation wells, for example, may improve contact between dissolved contaminants and remediation reagents. Funnel-and-gate systems were developed to improve the efficiency of *in situ* treatment, and can be cost-effective in some cases (Starr and Cherry, 1994).

Monitored natural attenuation (MNA) is generally considered too slow to provide effective containment at most chlorinated solvent sites, particularly when residual DNAPL is present (Wilson et al., 1994; McCarty et al., 1998). However, as pointed out earlier, while we have made progress in evaluating the potential for natural attenuation capacity, it is still_difficult to predict the conditions under which MNA can be effective.

At sites where source removal is anticipated, existing protocols (e.g., Wiedemeier et al., 1997) will require extensive post-treatment evaluation and monitoring to determine if MNA can be used.

3.3 Source Treatment

Chlorinated solvent source-zone remediation has consistently been identified by National Academy of Sciences reviews as one of our most difficult remediation challenges, with no proven technologies (NRC, 1994; NRC, 1997, NRC, 1999). The most recent study (NRC, 1999) concluded that "although a range of technologies is emerging to help clean up DNAPL-contaminated sites, the number of carefully controlled field tests is insufficient to establish the ultimate cleanup level attainable for each technology."

However, the recent development of more aggressive source-zone treatment technologies has caused a reevaluation of the conventional wisdom that DNAPL removal is very often "technically impracticable", and that long-term containment will be the most common remedial strategy. The source-zone technologies currently in use or in development include:

In Situ Destruction:

1. Enhanced Anaerobic Bioremediation
2. *In Situ* Chemical Oxidation
3. Metallic Catalyst Injection
4. *In Situ* Thermal Treatment
    a. Six-Phase Soil Heating
    b. Electrical Resistance Heating
    c. Radio-Frequency Heating

Removal:

1. Air Sparging/Vapor Extraction
2. Flushing
    a. Alcohol or Co-solvent Flushing
    b. Surfactant Flushing
    c. Cyclodextrin-Enhanced Flushing
3. Steam Injection (can also cause destruction)
4. Hot Water Injection

Clearly this is an extensive list, and many of the technologies listed above have several variations. Summaries of many of these technologies and the field trials that have been done to date are available in Fountain (1998) and the National Research Council review of groundwater and soil cleanup at DOE sites (NRC, 1998). However, there is currently no guidance for selecting which of these technologies to use at a specific site. Each has strengths and limitations, and all share fundamental limitations for treatment of specific DNAPL sites.

Of course, a broader issue is whether any of these technologies should be used at a specific site, and if so, what measures of success are appropriate. One significant issue that affects the decision to attempt source-zone remediation is our ability to locate and characterize DNAPL sources. Even minor heterogeneities can lead to extremely complex

migration pathways and localized entrapment (Dekker and Abriola, 2000, Kueper et al., 1993).

As a result, finding and quantifying the source area can be difficult, and delivering remedial agents to the sources can be extremely challenging. This difficulty in locating and accessing the residual DNAPL has contributed to the failure of many of the source removal technologies to achieve cleanup goals (e.g., Lowe et al., 1999; Fountain, 1998; Fountain et al., 1996; Saba et al., 2001, Fiorenza et al., 2000).

Even when sources can be located and accessed, there is considerable controversy regarding the impact of source removal technologies to improve groundwater quality and reduce overall plume management costs (e.g., Sale and McWhorter, 2001; Taylor et al., 2001; Enfield, 2000); Berglund, 1997). A key issue is the likely extent of any reduction in the contaminant mass flux as a result of source-zone remediation, and whether mass flux reduction is an acceptable cleanup goal (e.g., Einarson and Mackay, 2001; Feenstra et al., 1996). Although mass flux is the most commonly used term, flux should strictly be used for mass per unit area per unit time, which can be a difficult analysis (see Figure 1). As a result, "mass release rate" from a source (mass per unit time) may be the more proper term for what is actually measured in the field.

If mass flux or release rate is an acceptable measure of "success", measurement of mass flux will become an important issue. Measuring mass flux currently involves significant uncertainty (e.g., Wilson et al., 2000). The dissolved phase plume after treatment may still require containment, so integrated modeling and measurement of both the flux from the residual source and natural attenuation capacity of the subsurface environment will be essential (Chapelle and Bradley, 1998). To understand the natural attenuation capacity, the influence of source remediation technologies on natural attenuation processes needs to be understood, particularly since some of these technologies involve drastic changes in the subsurface environmental conditions.

As NAPL and dissolved contaminants migrate, the contaminants can diffuse into the surrounding matrix. This matrix diffusion can pose significant issues for remediation technologies, because these contaminants are difficult to remove, and can serve as a long-term reservoir (Parker et al., 1994). Thus, matrix diffusion needs to be understood and measured so that we can model and measure long-term mass flux accurately, and predict the effect of source treatment.

Our ability to model and predict DNAPL migration and remediation impacts is also questionable. Currently, very complex numerical models are used, with concomitant needs for computing power, user training, and long processing times (e.g., Falta et al., 1995; Delshad et al., 1996; Rathfelder et al., 2000). Remediation technologies can drastically affect the distribution of the DNAPL in ways that are not fully understood (e.g., Jawitz et al., 2000; Lowe et al, 1999; Udell, 1997). The predictive models available have not been sufficiently calibrated at the field level. Research to calibrate the models for DNAPL migration, dissolution, and the complex effects of remediation technologies is clearly needed. Further, simpler models useful to practitioners without extensive training and computer facilities would also be very helpful.

4.0 CAH SITE ISSUES

Given so many potential research questions, it is important to focus on those issues that are most critical and promise to make the most difference in the costs and efficacy of remediation. To assist in that prioritization effort, an initial list of key questions has been prepared. This summary is not complete and is intended as a starting point. Many of the questions raised are interrelated, and certainly others can and should be added. Nevertheless, the list is daunting, and the need to prioritize is clear. Focusing on those areas promising the most return on the R&D investments is essential for DoD's overall mission, as well as society's need to cost-effectively protect human health and the environment.

4.1 Characterization

Although this area is not a primary focus of the workshop, DNAPL sites remain difficult to characterize and there are several potentially important gaps in our basic scientific understanding. Our assumption is that cleanup technology development will have to operate within the current constraints of available characterization tools into the foreseeable future. The questions that need to be addressed in this area include:

1. For characterization of DNAPL sites, what is an acceptable level of accuracy for defining the extent of DNAPL in the subsurface?
2. How can we best evaluate proposed and existing characterization technologies?
3. Can we reduce the degree of uncertainty in establishing risk-based cleanup levels for these contaminants?
4. Is there a need for improved test methods for risk evaluations, particularly for ecological risk assessments?

4.2 Plume Remediation

A significant portion of the effort funded by SERDP and ESTCP has been devoted to cost-effective remediation of dissolved-phase plumes. The bulk of this effort has been related to natural bioremediation using anaerobic and/or cometabolic approaches. More recently, natural attenuation and passive containment have been emphasized as well. Given the state of the art and science:

1. Is this still a priority for research and/or technology demonstrations?
2. Are there other promising technologies that should be further developed or tested?
3. Which technologies are most promising at this point?

Other potential questions of concern relate to improving existing containment technologies. For example:

1. Is more work needed to understand the long-term effectiveness and economics of zero-valent iron walls, and can these be improved?
2. Do we have a sufficient understanding to develop guidance on optimizing pump-and-treat systems and is such guidance needed?

3. Do we have sufficient understanding of the many *in situ* bioremediation alternatives to develop guidance on technology selection and design?

A further area of emphasis in recent years has been improving the performance of *in situ* technologies by addressing the fundamental limitations. In particular:

1. Are technologies to enhance mixing in the subsurface still needed, and should this area remain a priority?
2. How should we test such mixing technologies, and what criteria should be used to measure success?

4.3 Source Treatment

The first issue is whether source removal should be pursued at all. The questions related to this area include:

1. Under what conditions should removal be attempted, and can we provide guidance on the value of source removal?
2. How do we appropriately and consistently evaluate the potential return on investment?
3. How should we measure success and how should we set the goals for a source removal action?
4. What criteria should be employed to select a source removal strategy, and to decide when to stop treatment?
5. For a specific site, or for sites in general, what is an appropriate definition of the regulatory term, "source removal to the extent practicable"?

Secondly, there are an increasing number of technologies available. Many have been tested to some extent and many others are in early developmental stages. We need guidance on:

1. Which technologies are most promising?
2. Which should be targeted for demonstration/validation, and which need more fundamental research and development?
3. What are the most critical specific issues and gaps in our understanding for each of the technologies being deployed or developed?

Thirdly, evaluating these technologies at reasonable scales is often very difficult. Questions include:

1. What factors should be considered in evaluating demonstrations and assessing performance?
2. What scales and site variables should be considered?
3. How serious is the potential for "rebound", and how long should monitoring be continued after active treatment?
4. What types of sites (and/or controlled facilities) should be used for testing these technologies?

5. What side effects should be considered in evaluating the technologies?

Finally, there are a series of questions regarding our understanding of the fundamental processes, which affects our ability to model and predict source treatment impacts:

1. How can we best model DNAPL transport within the subsurface, and the resulting mass flux of contaminants in the associated dissolved phase?
2. How important is matrix diffusion and how can we measure, model, and predict its impact on the potential for effective remediation?
3. What is the relative importance of understanding/monitoring "flux" or mass release rates versus point concentration measurements?

4.4 Technology Transfer

The ESTCP program in particular is interested in technology transfer, and the potential to increase DoD efforts in this area. The overall issue is whether DoD needs to increase its efforts in this area, and if so, how should it best be done? Questions include:

1. Is the knowledge base generated by R&D efforts being adequately transferred to consulting firms, regulators, and project managers?
2. Are technologies being used that do not work, or are they being used inappropriately because of lack of information?
3. Conversely, are new and more effective technologies not being accepted by regulators or practitioners because the information is not available?
4. What are the best methods to transfer new information and lessons learned from the DoD research programs?

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Attachment 1: CURRENT SERDP AND ESTCP PROJECTS

A listing of relevant project titles is provided below. Further information (including project descriptions, past projects, investigators, and status) is available on the SERDP and ESTCP web sites (www.serdp.org/ and www.estcp.org/).

CURRENT SERDP PROJECTS

Site Characterization

Negative Ion Sensors for Real-Time Downhole DNAPLs Detection

Non-Intrusive Characterization of Dense Non-Aqueous Phase Liquids Using Short-Lived Radiotracers in Partitioning Interwell Tracer Tests

Inexpensive Chemiresistor Sensors for Real-Time Ground Water Contamination Measurement

Shear-Horizontal Surface Acoustic Wave (SH-SAW) Chemical Sensors for *In Situ* Characterization and Monitoring of Trace Organic Contaminants in Aqueous Environments

Plume Remediation

***In Situ* Destruction**

Reactive Barriers

Competitive dechlorination

Influence of Groundwater Constituents on Longevity of Iron-Based Permeable Barriers

Evaluation of Performance and Longevity at DoD Permeable Reactive Barrier Sites

***In Situ* Bioremediation**

An Innovative Passive Barrier System Using Membrane-Delivered Hydrogen Gas for the Bioremediation of Chlorinated Aliphatic Compounds

Development of Effective Aerobic Co-Metabolic Systems for the *In Situ* Transformation of Problematic Chlorinated Solvent Mixtures

Aerobic and Anaerobic Transformation of cis-DCE and VC: Steps for Reliable Remediation

Factors Affecting cis-DCE and VC Biological Transformation Under Anaerobic Conditions

Characterization of the Aerobic Oxidation of cis-DCE and VC in Support of Bioremediation of Chloroethene-Contaminated Sites

Development of Permeable Reactive Barriers Using Edible Oils

Low-Volume Pulsed Biosparging of Hydrogen for Bioremediation of Chlorinated Solvent Plumes

Innovative Electrochemical Injection and Mixing Strategies for Stimulation of *In Situ* Bioremediation

Removal

<u>**Source Treatment**</u>

***In Situ* Destruction**

Foam Delivery of Hydrogen for Enhanced Aquifer Contacting and Anaerobic Bioremediation of Chlorinated Solvents

Removal

Aquifer Restoration by Enhanced Source Removal

CURRENT ESTCP PROJECTS

Site Characterization/Monitoring

Fiber Optic Biosensors
Direct Push Chemical Sensors
Radon 222 as a Natural Tracer
Flow and Transport Optimization Codes
Novel Natural Attenuation Analytical Technologies
Water and Solute Flux Measuring Device
Push-Pull Tests for Evaluating *In Situ* Aerobic Treatment

Plume Remediation

In situ Destruction

Bioremediation
Bioaugmentation (Anaerobic Treatment)
Treatability Test for *In Situ* Anaerobic Dechlorination
Cometabolic Air Sparging
Molasses Induced Reactive Zones

Monitored Natural Attenuation
Natural Attenuation in Wetlands

***In Situ* Chemical Treatment**
Injectable Nanoscale Bimetallic Particles
In situ Catalysis Using Pd Catalysts and Horizontal Flow Wells
In Situ Oxidation
Electrically Induced Redox Barriers

Removal

Air Sparging Multi-Site Evaluation

Source-Zone Treatment

In Situ Destruction

Bioremediation
Bioaugmentation for DNAPL Source Areas

Chemical Treatment

Sequential *In Situ* Chemical Oxidation and Bioaugmentation

Dynamic Underground Stripping with Hydrolysis Pyrolysis Oxidation

Removal

Surfactant Enhanced DNAPL Removal
Cyclodextrin-Enhanced *In Situ* Removal

Attachment D

DOD (Navy) Cleanup Program Macroview

S. Laura Yeh

Naval Facilities Engineering Service Center

Chlorinated Solvent Expert Panel Meeting

Chantilly, VA • August 6, 2001

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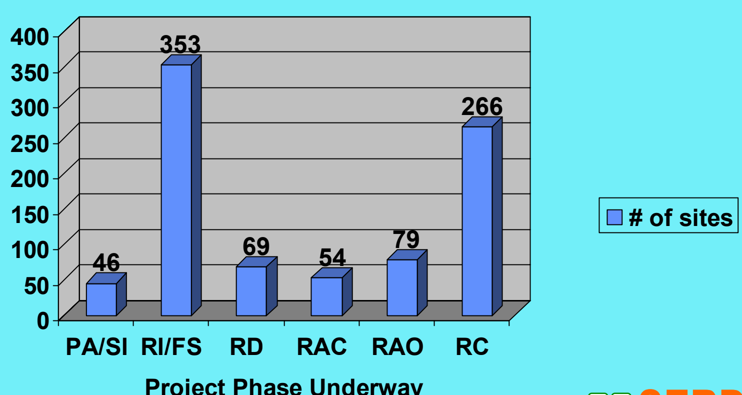
SERDP Strategic Environmental Research and Development Program
Improving Mission Readiness Through Environmental Research

Extent of Navy problem

The Navy has 867 chlorinated solvent sites at 242 installations.



Source: NORM Database, 2001

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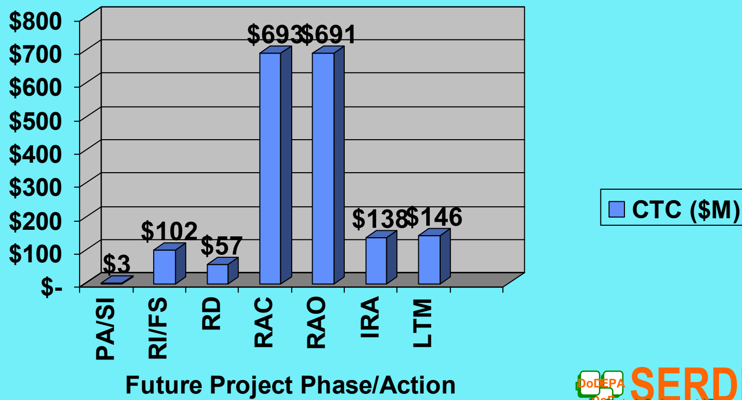
Cost to Complete by Project Phase/Action

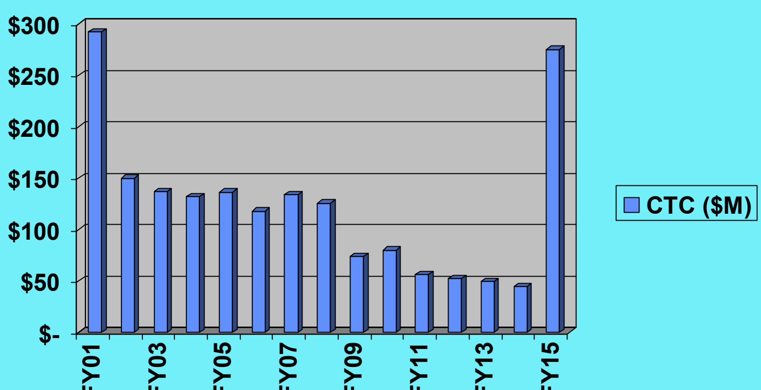
The projected cost to complete the 867 sites in future phases/actions from FY01-FY15 is $1,830M.



Source: NORM Database, 2001

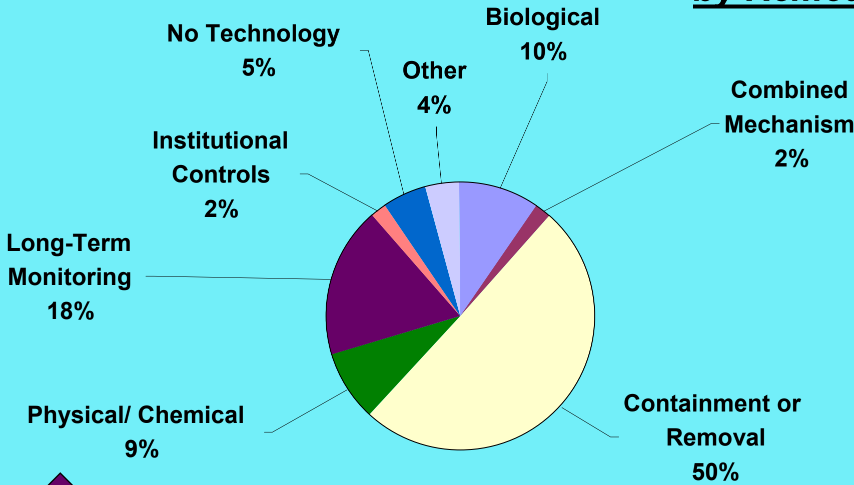
Cost to Complete by Funding Yr

The $1,830M may be broken out by FY as follows:



Source: NORM Database, 2001

Navy Chlorinated Solvent Sites by Remedy



Source: NORM Database, 2001

NOTE: Data provided by RPMs for the purposes of identifying funding requirements.

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Macroview Questions

- What are the issues and barriers to cleaning up chlorinated solvent sites within the DoD?
- What motivates the use and selection of source area technologies?
- How are performance standards defined for source area remediation technologies?

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Navy-wide issues: Regulatory/Community

- Getting approval for MNA/LTM
  - Difficult to shut down systems that are only treating the tail
  - MNA approval process is data intensive
- Unreasonable surface water discharge standards
  - No dilution policy
  - Default is MCLs
- Potential VC formation a barrier to use of enhanced bio methods
- Community perception where there is potential exposure via drinking water or land reuse (BRAC)

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Navy-wide issues: Technical

- Locating the plume in complex geologies (e.g. karst)
- Limitations to remediating sites with:
  - Silty sands and clays (including heterogeneous sites)
  - Fractured bedrock
  - Contamination at depth
- Better prediction on the likelihood of vinyl chloride formation for enhanced bio applications

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Navy-wide issues: Education

- Locating the source
  - What is DNAPL?/DNAPL migration and distribution concepts
  - What tools are available to delineate the hydrogeology?
  - What tools are available to identify DNAPL?
  - What is the proper level of DNAPL source area characterization for safe and effective remedial design?
- DNAPL removal technologies
  - What are the site-specific advantages/limitations?
  - What are the factors influencing cost and performance?

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Navy-wide Trends & Attitudes

- Aggressive source area removal driven by:
  - Property transfer (BRAC sites)
  - Human exposure pathway (buildings, drinking water)
  - Eco-risk (contamination next to wetlands)
- Source reduction viewed as a potential mechanism to get buyoff on MNA or LTM remedy
  - Some unrealistic expectations of meeting MCLs with source area remediation technology
  - Growing expectation to follow source removal with polishing step (bio, enhanced bio)
  - In most cases, focus is on meeting point of compliance downstream of source, rather than performance of remedial technology at the source

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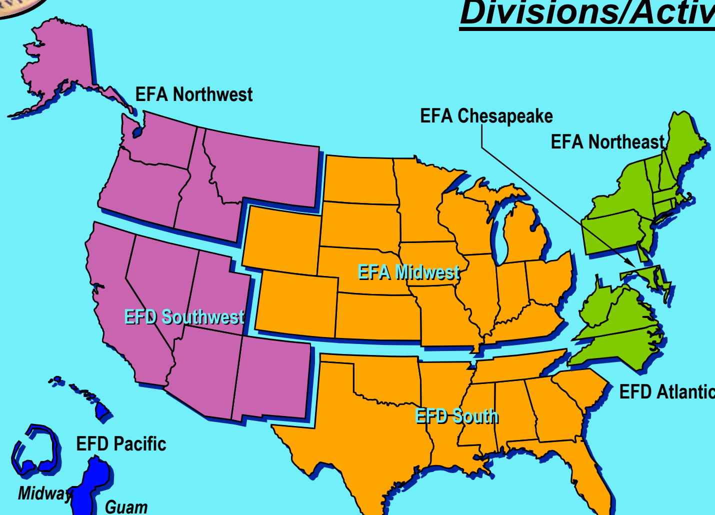
Navy-wide Trends & Attitudes (cont.)

- In-situ chemical oxidation increasingly favored by RPMs for dissolved-phase contamination in place of pump and treat
- Regarding the status of technology development for chlorinated solvent sites
  - High level of satisfaction among RPMs
  - Interest in continued technology development focusing on low perm and fractured bedrock sites
  - Additional cost & performance data is needed

Navy Engineering Field Divisions/Activities



Region-specific issues/findings: EFD Atlantic

- With 50% of sites in RA phase, administratively difficult to switch gears to innovative approaches
  - Hard to justify putting a site back to an "earlier phase" of the process for additional source area characterization, remedial design etc.
  - Reliable performance and cost data often not available to justify increased upfront funding needed for treatability studies, pilot demos, etc.
  - RPMs feel locked into remedial approaches by cost budgeting process

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Region-specific issues/findings: EFD South

- Remediation of DNAPL sites with low perm soils/clays a challenge
- Remedy selection driven by estimates of remediation timeframes
  - Unrealistic timeframes attached to pump and treat
  - Estimating timeframe for MNA requires estimating subsurface contaminant mass -- difficult to do
  - Software tools needed and under development
- Optimized p&t system cost example: 700 gpm, 7 wells, 4 air-strippers, $250,000/yr O&M (GOCO facility)

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Improving Mission Readiness Through Environmental Research

Region-specific issues/findings: EFD NorthEast

- **Fractured bedrock sites a challenge**
  - Approximately 1/3 chlorinated solvent sites are in fractured bedrock
  - Current remedy of choice is pump and treat
  - 1 chem ox project underway and another planned at a fractured bedrock site
- **MNA example: $M spent doing a 3-year interim study to obtain buyoff on shutting down p&t system for MNA despite negative impacts of p&t system on a wetlands area**

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Region-specific issues/findings: EFA Chesapeake

- **Example of community perception issue at BRAC facility:**
  - Deep aquifer a drinking water source, but not contaminated; upper aquifer is contaminated (150 ppb TCE at property line)
  - Two residences at southern border of Navy property where contamination going off-site
  - To handle perceived threat to drinking water, Navy put both residences on potable water network and installed a p&t system for upper aquifer as an IRA
  - At another site, where a new building is to be constructed over ≤300 ppb TCE plume, tenants-to-be are challenging Navy and EPA risk assessment results

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Region specific issues/findings: EFA NorthWest

- Community acceptance of proposed remedial solutions is the main issue.
- Difficulties delineating the groundwater plumes because of the complex geology.
  - Example: Puget Sound Naval Shipyard has 340 acres of tideland with 11,000 feet of shoreline. Although chlorinated solvent groundwater is discharging to the Sound, and there is a known source upgradient, between the geologic complexity and dry dock pumping operations which are diluting the groundwater, the regulators have agreed to LTM remedy.

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Region specific issues/findings: EFD Pacific

- Chlorinated solvent contamination a minor problem (only 2 sites)
- Cost example for remedial activities at dry-cleaning facility:
  - 4 acre facility with 1/4 acre source, ~1.5 acre on-site chlorinated solvent plume
  - At source: tank and waste soil removal + SVE for vadose zone contamination(to 65 ft bgs)
  - 18 on-site monitoring wells, with 13 currently being sampled
  - No remedy in place for dissolved-phase contamination but biotransformation of chlorinateds is naturally occurring at source -- currently discussing MNA remedy with EPA IX
  - Total cost to date ~$4M

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Region specific findings/issues: EFA SouthWest

- Regulators very aggressive about "finding the source"
  - request DNAPL investigations even when past site activities and groundwater concentrations do not warrant it
  - lack of understanding of how to find DNAPL
  - false perception that DNAPL exists mostly in "pools"
  - chasing DNAPL source areas a big cost driver
- Where DNAPL investigations warranted, helpful to consider specific requirements of remedial technology (i.e. recommend a phased approach)

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Region specific findings/issues: EFA SouthWest (cont.)

- Compliance with California Environmental Quality Act (CEQA) is burdensome
  - 60+ day review period
  - involvement with document review of EE/CA* through remedial action operations
- Surface discharge issue example: At NAS North Island in San Diego Bay, regulators want to use center-of-plume contaminant concentrations to calculate eco-risk for what is discharging to the bay -- more realistic exposure scenarios needed

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*EE/CA = engineering evaluation/cost analysis

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Acknowledgements

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- EFD Pacific - Debbie Loo, Peter Nakamura, Darlene Ige
- EFA NorthWest - Larry Tucker, Cindy O’Hare
- EFD Atlantic -- Kate Landman
- EFA Chesapeake - Walter Legg, Shaun Jorgensen

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Attachment E

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

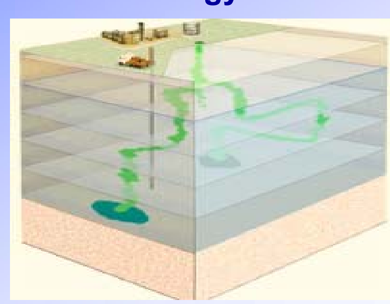
Where we are

Where we want to be

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

- **Every site is different-- there is not, and never will be a "silver bullet" technology for difficult DNAPL sites.**



Issues with Chlorinated Organics Remediation at DoD Sites

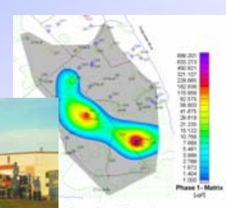
A Field Perspective

- USACE Environmental Restoration Support
  - Army Installation (IRP)
  - Formerly Used Defense Sites (FUDS)
  - Army Base Realignment & Closure (BRAC)
  - Selected Superfund Site work for US EPA
  - Work for others by request - AF, FAA, etc
  - Formerly Utilized Sites Remedial Action Program (FUSRAP)

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

- Contaminants Commonly Found at Remediation Sites:
  - Explosive Wastes
  - **Solvents**
  - Hydrocarbons
  - Metals
  - Rad Wastes
  - **Others such as PCBs, SVOCs, and Pesticides**



Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

EPA's Programmatic Expectations for Ground Water and Objectives for Site Response Actions at CERCLA Sites

"EPA expects to return usable groundwater to their beneficial uses wherever practicable, within a timeframe that is reasonable given the particular circumstances of the site. When restoration of ground water to beneficial uses is not practicable, EPA expects to prevent further migration of the plume, prevent exposure to the contaminated groundwater, and evaluate further risk reduction."

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

Pump and Treat - SVE, Air Sparging - Source Removal

80's 90's 00's

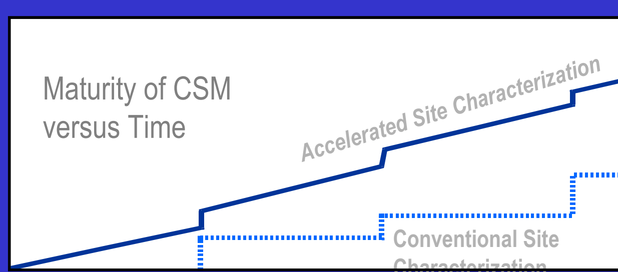
- Influent concentrations at treatment showing downward trend then stabilizing – residual DNAPL long-term mass removal limitation
- Pump & treat for hydraulic control with targeted integrated system for source/mass removal
- Recognized need for supplemental characterization to validate remediation and redirect optimization

Issues with Chlorinated Organics Remediation at DoD Sites

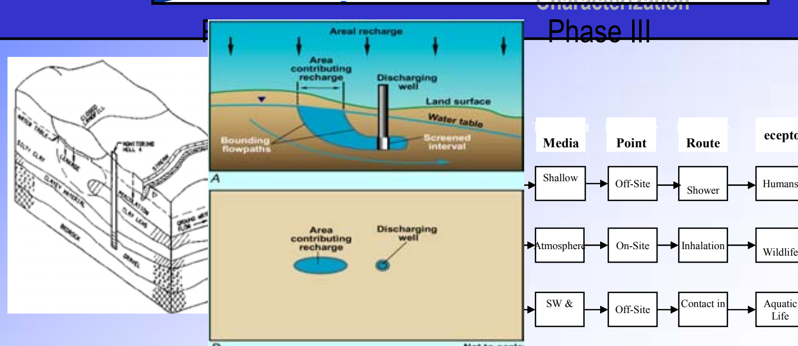
A Field Perspective

Development of the CSM

Conceptual Model Maturity



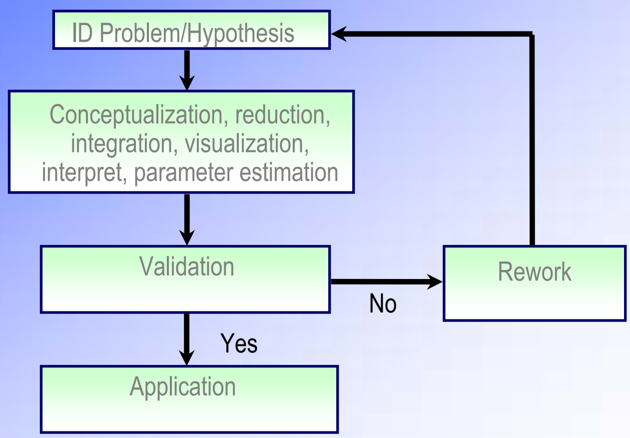
Phase III



Issues with Chlorinated Organics Remediation at DoD Sites

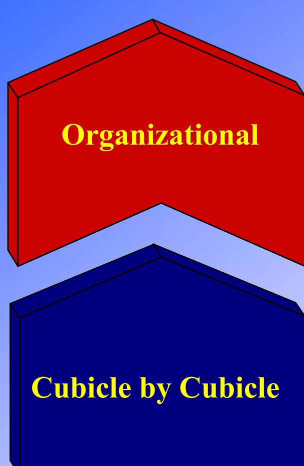
A Field Perspective

Cycle of Development



Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective



ITRC, 1997

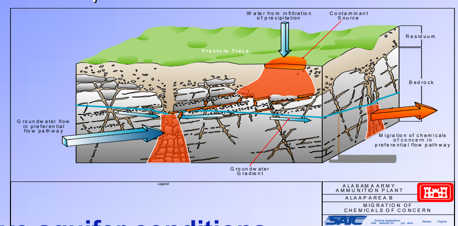
Characterization and long term monitoring

- Concerns about the accuracy, reliability, comparability are raised with some of the field-based analytical tools
- Expect dynamic work plans, field-based analytical and systematic planning will guide the way data is collected and analyzed during future site clean-up activities
- Institutionalize newer proven approaches
- DNAPL Characterization Methods and Approaches, Kram, et al, 2001

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

Technical feasibility is a concern:



~27% of Army Installations have aquifer conditions making aquifer restoration technically impracticable

Concerns are not only increasing costs but whether available technologies can achieve plume containment and source control in complex hydrogeologic systems

Issues with Chlorinated Organics Remediation at DoD Sites

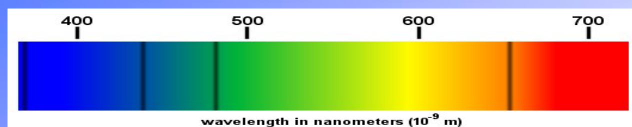
A Field Perspective

Factors Contributing to High Costs and Failures

- Lack of Knowledge of Subsurface Conditions
- Operational and Subsurface Data Collected - Not correctly evaluated
- Significant changes in site funding, conditions or regulatory criteria
- Accurately relating the information to remedial action objectives
- Unclear closure objectives

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective



Dissolved | *Co-mingled* | *Residual Saturation*

- Pour product of the core when it is removed above residual saturation

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

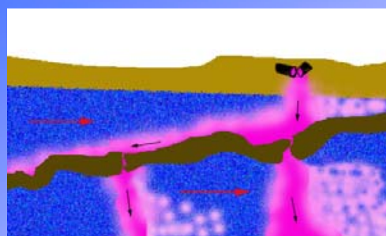
– Using RAOs, How to define and evaluate target areas of treatment “source removal” and related them back to risk reduction?

– What level of spending is acceptable for amount of risk reduction?

– How do we re-evaluate and reprogram for risk reduction with incremental improvements on ongoing projects?

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective



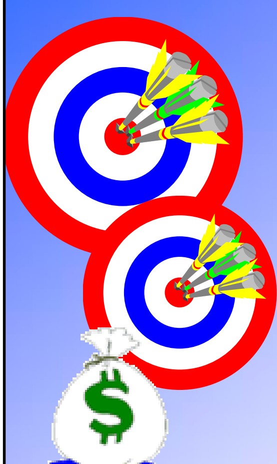
Virginia Tech, 1996

Planning for Uncertainty

- Manage uncertainty reduction (data collection) with impact mitigation (use of contingencies).
- For ground water
  - Early warning monitoring system
  - Mitigate adverse impacts

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective



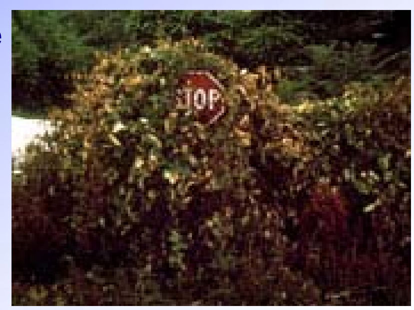
- Project performance is measured by:
  - **Budget execution, time**
  - **Baseline for comparison on process improvement is a moving target**
- Innovative technologies selected when difficulties with conventional technology arise
- Need to incorporate life-cycle cost, technology treatment efficiency & effectiveness
- Present worth cost to compete of a remedial action may not support aggressive remediation but favor long-term monitoring, natural attenuation or containment to show risk reduction for funds invested

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

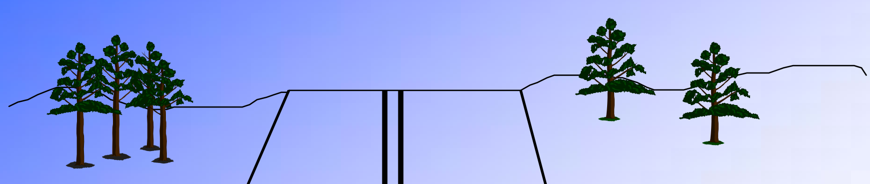
Determining Process End Goals

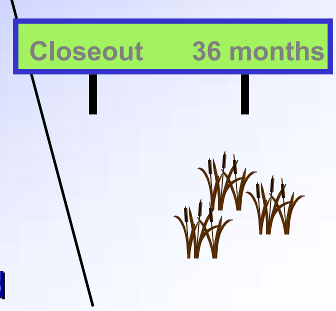
- Define the decisions that must be made
- Develop decision rules
- ID data necessary to support decision making
- Determine limits on decision errors



Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective





- **Site closure is a process not an endpoint**
  - **Institutional Controls**
  - **5-year reviews**
- **Clearly identify when cleanup actions will be modified or stopped**

Issues with Chlorinated Organics Remediation at DoD Sites

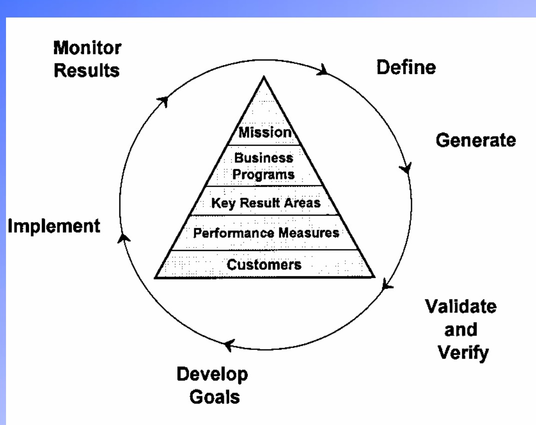
A Field Perspective

Vendor/Contractors/Consultants Issues:

- Technology is oversold
- Risky - “Not conventional, tried and true”
- Government purchases vendor specific patented services that are not well understood, need to increase understanding
- Safety Issues –release of vapors and migration of NAPL
  - (in-situ chemical oxidation, thermal)
- Diminish the philosophy “We tried it once and it doesn’t work” --leading to a categorical dismissal of technology for future projects
- Create a more competitive climate for contractor selection that includes IT for DNAPL monitoring & treatment

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective



•Apply the best innovative class of technology when and where it makes sense

•Validate and verify what we do, improve operations, data reliability, quality and efficiency measure (unit cost)

•Reduce O & M lifecycle $, (interruptions, or backups or redundancies)

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

- Field measurement technologies provide results that are faster, less expensive, and at times provide results unobtainable with standard off-site methods
- Encourage use of multiple technologies & tools for characterization and remediation of DNAPL sites
- Interagency clearing house of lessons learned to evaluate effectiveness

Issues with Chlorinated Organics Remediation at DoD Sites

A Field Perspective

- Focus attention away from technologies requiring significant O& M
- Provide optimization checklists to reduce capital and annual (O&M) costs and include in the cost estimate for a remedial action alternative
- Focus on treatment of contaminant source
- Educate on technical impracticability

What can ESTCP & SERDP do?

–Develop, demonstrate and improve

- – knowledge of DNAPL monitoring techniques to improve robustness, acceptance
- – performance monitoring
- – in-situ source removal technologies
- – improve safety & performance and understand of existing remedies
- – determine level of treatment necessary to reduce risk

Attachment F

Compilation of Actual and Potential In-Situ Thermal Treatment Projects

Actual Projects

Project	Contaminant (s)	Technology	Status
LLNL Gas Pad	Gasoline	Steam Injection	Complete (115,000 lbs recovered)
Visalia Pole Yard, NPL Site	Creosote/Pentachlorophenol	Steam Injection	Ongoing Full-Scale (1 million lbs recovered in 18 months)
Skokie, IL	Trichloroethylene (TCE)	6-Phase Heating	Full-Scale Cleanup Completed
Seattle, WA	Tetrachloroethylene (PCE)	6-Phase Heating	Full-Scale Cleanup Completed
Ft. Richardson, AK	Tetrachloroethane	6-Phase Heating	Full-Scale Cleanup Completed
Atlanta, GA	Kerosene	6-Phase Heating	Full-Scale Cleanup Completed
Portland, IN	Tetrachloroethylene (PCE), Trichloroethylene (TCE)	In-Situ Thermal Desorption (ISTD)	Full-Scale Cleanup Completed
Tanapag, Saipan, NMI	Poly Chlorinated Biphenyls (PCB)	Thermal Blanket	Full-Scale Cleanup of 1st Phase Completed
Tanapag, Saipan, NMI	Poly Chlorinated Biphenyls (PCB)	In-Situ Thermal Desorption (ISTD)	Ongoing
Fuel Terminal, Eugene, OR	Diesel Fuel	In-Situ Thermal Desorption (ISTD)	Full-Scale Cleanup Completed
Naval facility, Ferndale, CA	Poly Chlorinated Biphenyls (PCB)	In-Situ Thermal Desorption (ISTD)	Full-Scale Cleanup Completed
Drag strip, Glens Falls, NY	Poly Chlorinated Biphenyls (PCB)	In-Situ Thermal Desorption (ISTD)	Demonstration Project Completed

Project	Contaminant (s)	Technology	Status
MEW, Cape Girardeau, MO	Poly Chlorinated Biphenyls (PCB)	In-Situ Thermal Desorption (ISTD)	Demonstration Project Completed
Navy BADCAT, Vallejo, CA	Poly Chlorinated Biphenyls (PCB)	In-Situ Thermal Desorption (ISTD)	Demonstration Project Completed
Cincinnati, OH	Gasoline/Diesel	6-Phase Heating	Pilot Scale Completed
Fairbanks, AK	Gasoline/Diesel	6-Phase Heating	Pilot Scale Completed
Fairbanks, AK	Gasoline/Diesel	RF Heating	Pilot Scale Completed
Lemoore NAS, CA	JP-5	Steam Injection	Full-Scale Cleanup Completed
Petrochemical, TX	Solvents	3-Phase electrical heating	Sequential Full-Scale Cleanup of Hot Spots
NAS North Island, San Diego, CA	Trichloroethylene (TCE), JP-5	In-Situ Thermal Treatment	Full-Scale Cleanup Underway Following Successful Pilot
Yorktown Navy Facility, VA	Fuel Oil	In-Situ Steam heating	Full scale Project Underway. Steam in Pipes Used to Reduce Viscosity to Facilitate Recovery in Trenches
Rainbow Disposal, Huntington Beach, CA	Diesel Fuel	Steam Injection	EPA Site Demonstration
DESC, Whittier, AL	JP-5	Steam Injection	Full-Scale Design and Construction
Bulk Oil Plant, Jacksonville, FL	Motor Oil	Steam Injection	Full-Scale Design/Start up Fall 2000
Metal Recycling Facility, Boston, MA	Heavy Machine Oil	In-Situ Thermal Treatment	Procurement and Fabrication Underway
Aircraft Engine Plant, Lynn MA	Poly Chlorinated Biphenyls (PCB)	Steam Injection	Design Completed/Implementation 2001

Project	Contaminant (s)	Technology	Status
Safety Kleen, Breslau, Ontario	Poly Chlorinated Biphenyls (PCB)	In-Situ Thermal Treatment	Pilot Test
DESC, San Pedro, CA	Diesel Fuel	In-Situ Thermal Treatment	Pilot Test
PSNS, Bremerton, WA	Fuel Oil	In-Situ Thermal Treatment	Pilot Test
Ft. Hood, TX	JP-8	Steam Injection and 3-Phase Heating	Demonstration
Panama City, FL	Diesel Fuel	Steam Injection	Full-Scale
Plating Facility, Danbury, CT	CVOCs	Steam Injection	Full-Scale Designed and Constructed
DOE Savannah River, SC	Tetrachloroethylene (PCE), Trichloroethylene (TCE)	Steam Injection	IWR Ongoing
A.G. Communications North Lake, IL	Solvents	Steam Injection	Ongoing
Waukegon, IL	Methylene Chloride	6-Phase Heating	Full-Scale Cleanup Completed
Portland, OR	Trichloroethylene (TCE)	6-Phase Heating	Full-Scale Cleanup Ongoing
Newark, CA	Ethylene Dibromide (EDB)	6-Phase Heating	Pilot Project
Air Force Plant 4, Ft. Worth, TX	Solvents	6-Phase Heating	Pilot Project Completed, Full-Scale Design Contracted
Paducah GDP, KY	Trichloroethylene (TCE)	6-Phase Heating	Pilot Project In Design
Charleston Navy, SC	Tetrachloroethylene (PCE)	6-Phase Heating	Full-Scale Project In Design

Project	Contaminant (s)	Technology	Status
Holyoke, MA	Styrene	Steam Injection	Ongoing
Alameda NAS	Trichloroethylene (TCE), Diesel, Motor Oil	Steam Injection	Pilot Project Completed
DOE Portsmouth, OH	Trichloroethylene (TCE)	Steam Injection	Pilot Project Completed
Solvent Services, San Jose, CA	Chlorinated Solvents	Steam Injection	Pilot Project Completed
Port of Ridgefield, WA	Polycyclic Aromatic Hydrocarbon (PAHs), Pentachlorophenol (PCP)	Steam Injection	Contract Awarded
Cape Canaveral, FL	Trichloroethylene (TCE)	Steam Injection, Oxidation, 6-Phase Heating	Joint DoD/DOE/EPA/NASA "Treat Off"
Mobil Oil	Petroleum	RF Heating	Full-Scale Completed
Ashland Refinery, St. Paul, MN	Petroleum	Microwave Heating	Full-Scale Completed
Wyckoff Wood Treater, NPL Site	Creosote/Pentachlorophenol (PCP)	In-Situ Thermal Treatment	Signed ROD, Conceptual Design Underway
Rocky Mt. Arsenal Hex Pit, Commerce City, CO	Pesticides	In-Situ Thermal Desorption (ISTD)	Full-Scale Design/EPA SITE Demonstration
Pole Yard, Alhambra, CA	Creosote/Polycyclic Aromatic Hydrocarbons (PAHs)	In-Situ Thermal Desorption (ISTD)	Under Contract
N Ryan St. Site, Lake Charles, LA	Polycyclic Aromatic Hydrocarbons (PAHs), Poly Chlorinated Biphenyls (PCBs)	In-Situ Thermal Desorption (ISTD)	Administrative Order on Content Action Memorandum Issued

Project	Contaminant (s)	Technology	Status
Potential Sites			
McCormick and Baxter Wood Treater NPL	Creosote	In-Situ Thermal Treatment	Addional Site Characterization Underway
Loring AFB	Trichloroethylene (TCE) in Fractured Bedrock	Steam Injection	DoD Has Budgeted FY2000 Funding for Pilot
Ft. Lewis, WA	Trichloroethylene (TCE)	In-Situ Thermal Treatment	Potential Army-Funded Demonstration
George AFB	Jet Fuel	In-Situ Thermal Treatment	"Candidate" Site
Williams AFB	Jet Fuel	In-Situ Thermal Treatment	"Candidate" Site - FS Underway SITE Program Proposal
Calhoun Park, SC	Polycyclic Aromatic Hydrocarbons (PAHs)	In-Situ Thermal Treatment	Ongoing Discussion with RP
Naval Shipyard, Yorktown, VA	Fuel Oil	In-Situ Thermal Treatment	Procurement Planned
Air Warfare Center	Trichloroethylene (TCE), Tetrachloroethylene (PCE) and VE	In-Situ Thermal Treatment	EE/CA in Place, Removal Planned
Guadalupe Oil Field	Refinery Products	Steam Injection	Panel has Recommended Horizontal Well Pilot
Romic, CA	VOCs/SVOCs	Steam Injection	Proposed for SITE Demonstration
Rocketdyne Simi Valley	Trichloroethylene (TCE) in Fractured Media	Steam Injection	Preliminary Discussions with EPA R9 and Cal EPA
Mandan, ND	Diesel	Microwave Heating	Demonstration Project Under Discussion
Albuquerque, NM	Creosote	In-Situ Thermal Treatment	Initial Discussion with RPM
Pt. Huenume, CA	Misc	Steam Injection	Approved as ESTCP Project

Project	Contaminant (s)	Technology	Status
Lowry Landfill	VOCs/SVOCs	6-Phase Heating	Full Scale Design
Taylor Lumber	Creosote, Polycyclic Aromatic Hydrocarbons (PAHs)	In-Situ Thermal Treatment	Initial Discussion with OSC
American Creosote	Creosote, Polycyclic Aromatic Hydrocarbons (PAHs)	In-Situ Thermal Treatment	Initial Discussion with OSC
Edwards AFB	Solvents in Fractured Media	In-Situ Thermal Treatment	Proposed SITE Demonstration Project
Kaufman and Minteer (EPA R2)	Trichloroethylene (TCE)	6-Phase Heating	FS Stage
Williams AFB	Jet Fuel	Steam Enhanced Extraction	Recommended for Site Demonstration by AZ DEQ
Beede Waste Oil	Solvents and PHCs	Steam Enhanced Extraction	Conceptual Design Presented to EPA's Remedy Review Board 11/2000
Texarkana Wood	Creosote, Polycyclic Aromatic Hydrocarbons (PAHs), Pentachlorophenol (PCP)	In-Situ Thermal Treatment	Initial Discussions with Federal and State RPMs